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Thermal desorption mass spectrometry of alkali metal atoms from transition metal surfaces. The influence of coadsorbed oxygen

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The coverage dependence of the activation energy of desorption for a planar array of electrical dipoles has been calculated in order to understand thermal desorption traces of alkali metal atoms from transition metal surfaces. The successful comparison between the computed spectra and available experimental data for K/Fe(110), K/Fe(100), K/Fe(polycrystalline), and K/Pt(111) allows us to demonstrate that the mutual dipolar repulsion within the adlayer is responsible for the coverage dependence of the thermal desorption spectra (TDS) characteristic of the above mentioned systems. Shifts of the TDS peaks up to about 450 K due to the lowering of $\sim 50\%$ in the energy of desorption are well described by the proposed model. Based on these results a simple and accurate method to assess the coverage dependence of the desorption energy is presented. The coadsorption of electropositive and electronegative atoms has been modeled assuming a planar array of electrical dipoles of opposite directions. It is demonstrated that oxygen atoms substantially reduce the repulsion energy on the alkali adlayer which becomes thermally stabilized in agreement with published experimental results. In fact, for the systems K + O/Fe(polycrystalline) and K + O/Pt(111) the onset of K desorption is found to be shifted by about 200 K due to the presence of coadsorbed oxygen atoms.

I. INTRODUCTION

The study of the adsorption of alkali metals on transition metal surfaces has recently attracted growing attention. These systems have been thoroughly investigated by a great variety of experimental techniques¹⁻¹⁶ and many independent workers have also studied theoretically the subject.¹⁷⁻²¹ Three main reasons strongly support these efforts; (i) alkali adsorption enhances the electron-emission properties of a surface,^{1,3-7,13,16,22} (ii) the addition of small amounts of alkali (or) and alkali compounds on transition metal surfaces is known to have enormous effects on the selectivity and reactivity of some heterogeneously catalyzed reactions, i.e., the so-called promotion effect,^{6,8,9,12-16,23-27} and (iii) theoretical interest also arises because these systems may be considered as one of the simplest examples of chemisorption.^{4,17}

The classical model for the chemisorption of alkalis on transition metals proposed by Langmuir in 1932 is based on the assumption that the alkali atom transfers its valence s electron completely to the metal substrate (Refs. 17 and 21 and references therein). This early picture has already been modified in 1935 in the quantum-mechanical treatment by Gurney who shows that the ionization is incomplete (an excellent review of the works of Langmuir and Gurney can be found in Ref. 21). Also the "jellium" model proposed by Lang yields incomplete charge transfer.¹⁷ Recently quantum-mechanical all-electron local-density calculations show that charge redistribution upon Cs adsorption on W(001) takes place essentially outside the surface W atoms and that the observed lowering of the work function is mainly due to the polarization of Cs valence electrons toward the W surface. Furthermore, experimental verification of partial occu-

pation of the $4s$ valence level of K adsorbed on Cu(110) has recently been reported.¹⁴ Therefore, the alkali-substrate complex can be treated as an electrical dipole taking the interaction with the surrounding dipoles into account. In fact, this statement is supported among others, by the following experimental results: (i) as the surface coverage is increased the dipolar repulsion becomes appreciable in LEED patterns.^{2,10,13} (ii) Mutual depolarization effects in the adlayer are also manifested in the alkali induced work function changes of transition metal surfaces.^{1,3-7,13,16,22,29} (iii) The dipolar interaction is also evidenced in the coverage dependence of the thermal desorption mass spectra (TDS) recorded subsequently to the adsorption of alkali atoms. The common feature of these spectra is the dramatic shift of the desorption maxima toward lower temperatures when the surface concentration is increased.^{3,5-7,9,10,13} A further support arises from the successful description of the alkali induced work function lowering based on the well known Topping model.^{1,7,22,28,29}

The aim of this work is to propose (see Sec. II A) and discuss (see Sec. II B) a model which accounting for the dipolar interaction between adatoms, could be able to explain the TDS of alkali metals from transition metal surfaces. The model is successfully compared with available experimental data found in the literature for the systems K/Fe(110), K/Fe(100), K/Fe(poly), and K/Pt(111) (see Sec. II B). In Sec. II C a simple method to assess the coverage dependence of the desorption energy is proposed and discussed. In Sec. III A, the model is further extended in order to describe the influence in the TDS of alkali atoms caused by the coadsorption of electronegative species. It is shown that the addition of oxygen thermally stabilizes the alkali in agreement with experimental results recently pub-

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lished.^{6,10} This effect would likely be important for the long time conservation of the optimal concentration of the electronic promoters in real catalytic processes under stationary conditions.^{6,10} Remarkably, based on the same guideline we have previously demonstrated that under certain circumstances the coadsorption of alkali and oxygen atoms further enlarged the electron emission from surfaces²⁹ in agreement with experimental results.^{6,11,30}

II. DESORPTION OF ALKALI ATOMS FROM TRANSITION METAL SURFACES

A. The model

The rate of desorption $\{R(N, T)\}$ of alkali metal atoms from a metal surface may be written as^{3,10}

$$R(N, T) = -dN/dt = \nu_0 N \exp[-E_D(N)/RT], \quad (1a)$$

where N is the number of adsorbed atoms per unit surface area, ν_0 is the pre-exponential factor of the desorption rate, T is the absolute temperature, R is the gas constant, and $E_D(N)$ is the activation energy of desorption. Note that ν_0 is assumed temperature and coverage independent.^{3,5,7,10} TDS experiments are usually performed increasing uniformly the temperature of the sample, i.e.:

$$T = T_0 + \beta t, \quad (1b)$$

where β is the heating rate and T_0 is the temperature of the sample at $t = 0$.

The activation energy can be rewritten as

$$E_D(N) = E_D(N=0) - E_R(N), \quad (2)$$

where $E_D(N=0)$ is the desorption energy in the limit of zero coverage, i.e., when the lateral interactions between adsorbed particles can be neglected and $E_R(N)$ accounts for the coverage dependent repulsive energy in the adlayer.

In order to evaluate $E_R(N)$ it has been assumed, as stated earlier, that the adsorbed atom can be treated as a polarizable entity with a dipole moment of magnitude $P(N)$ pointing away from the surface^{4,18,19,29} and a constant polarizability (α).

Due to the strong repulsive forces between adsorbed alkali atoms the average distance between nearest neighbor adatoms (r_s) is maximum, i.e., the adparticles are uniformly spaced.^{2,13} Under this assumption and for an hexagonal array it follows that²⁹

$$r_s = (4/3)^{1/4} \cdot N^{-1/2}. \quad (3)$$

For the same array, the depolarization field $\{\epsilon_d(N)\}$ acting on the individual dipoles is given by²⁹

$$\epsilon_d(N) = -P(N) \cdot \sum_{n=-\infty}^{+\infty} \sum_{m=-\infty}^{+\infty} (n^2 + m^2 - nm)^{-3/2} r_s^{-3}, \quad (4)$$

where n and m are integral numbers which cannot be equal to zero simultaneously. Performing the double summation of Eq. (4) according to Topping³¹ it follows that

$$\epsilon_d(N) = -P(N) \cdot 9 \cdot N^{3/2}. \quad (5)$$

Since each adparticle is partially depolarized by ϵ_d its dipole moment is then given by²⁹

$$P(N) = P(N=0)/\{1 + 9\alpha N^{3/2}\}, \quad (6)$$

where α is the effective polarizability of the adalkali-substrate complex and $P(N=0)$ is the dipole moment of an isolated adatom. Due to its position in the field created by the surrounding adparticles, each dipole has a potential energy $E_R(N) = -P(N) \cdot \epsilon_d(N)$ which can be evaluated using Eqs. (5) and (6). Hence,

$$E_R(N) = 9 \cdot P(N=0)^2 N^{3/2} / (1 + 9\alpha N^{3/2})^2. \quad (7)$$

Insertion of Eq. (7) into Eq. (2) gives explicitly the dependence of the activation energy of desorption on coverage and can be used in connection with Eq. (1) to evaluate the desorption rate.

At this point it is useful to acquaint the reader with the main features of the model, the magnitude of the involved

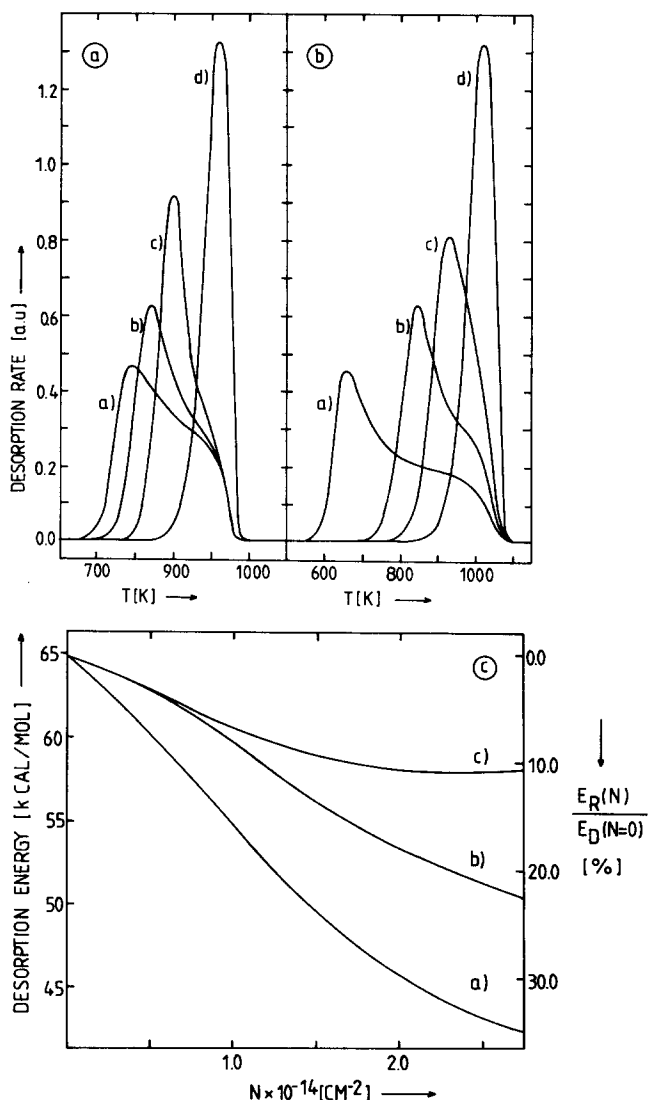


FIG. 1. (a) and (b). Thermal desorption traces calculated for some typical values of the relevant parameters of the model. (a) Computed desorption rates taking $P(N=0) = 7$ D and (a) $\alpha = 10$ Å³, (b) $\alpha = 15$ Å³, (c) $\alpha = 25$ Å³, and (d) $\alpha \rightarrow \infty$. (b) Calculated desorption rates taking $\alpha = 15$ Å³ and (a) $P(N=0) = 10$ D, (b) 7 D, (c) 5 D, and (d) 0.0 D. (c) The coverage dependence of the desorption energy for the following values of the relevant parameters: (a) $P(N=0) = 10$ D, $\alpha = 15$ Å³, (b) $P(N=0) = 7$ D, $\alpha = 10$ Å³, and (c) $P(N=0) = 7$ D, $\alpha = 25$ Å³. The right ordinate indicates the repulsion energy relative to the desorption energy in the limit of zero coverage [$E_D(N=0) = 65$ kcal/mol].

TABLE I. Dipole moment $\{P(N=0)\}$ and activation energy of desorption in the limit of zero coverage $\{E_D(N=0)\}$ for various alkali/transition metal systems. The values of $P(N=0)$ obtained applying the Topping model for the alkali induced work function changes {row 3} may be compared with the results of the present work {row 4}. Reported values of $E_D(N=0)$ obtained evaluating thermal desorption experiments {row 5} are compared with the results of the present work {row 6}.

		Na/Ni(111) Na/Ni(100) Reference 3	K/Fe(100) Reference 7	K/Fe(110) Reference 7	K/Fe(poly) Reference 6	K/Pt(111) ...	Cs/W(110) ...
$P(N=0)$	Topping model	7.2, 7.4	4.6	6.5	~5	9.4	14.6, 17
(D)	TDS model	7.3	7.5	8.5	8.1	Ref. 26	Refs. 4 and 21
$E_D(N=0)$	Expt	58	54 ± 2	57 ± 2	...	11.5	15.0
(kcal/mol)	TDS model	58.0	52.0	61.0	54.0	65	71.5
						Refs. 9 and 10	Ref. 5
						63.7	73.0

parameters, the shape of the spectra, etc. Hence, Figs. 1(a) and 1(b) show the effect of the lateral repulsive interactions on the computed desorption rate using reasonable values for the relevant parameters of the model.²² All these results have been evaluated by taking the same initial surface concentration $\{N_0\}$ of $N_0 = 2.7 \times 10^{14} \text{ cm}^{-2}$, which can approximately be estimated to be about one-half monolayer for most cases.^{5,7,10,13,16} As it is clearly evidenced in the figures, the sharp and slightly asymmetric peak characteristic of a first order reaction without lateral interactions is considerably influenced by the repulsion forces acting on the adlayer.

Figure 1(c) shows the dependence of $E_D(N)$ with coverage for some values of α and $P(N=0)$ also used in Figs. 1(a) and 1(b). The repulsion energy relative to the activation energy of desorption in the absence of interaction $[E_R(N)/E_D(N=0)]$ has also been included in the right

ordinate of Fig. 1(c).

For relatively weak repulsive interaction $[P(N=0) \lesssim 7 \text{ D}$ and $\alpha \gtrsim 15 \text{ \AA}^3$, i.e., $E_R(N)/E_D(N=0) \lesssim 15\%$ in Fig. 1(c)] the desorption peaks are shifted to lower temperature (displacement by up to 150 K) while their intensity decreases by a factor 2 at the most. The presence of a shoulder in the high temperature tail of the desorption traces can also be distinguished. For stronger repulsion energy $[P(N=0) \gtrsim 7 \text{ D}$ and $\alpha \lesssim 15 \text{ \AA}^3$, i.e., $15\% \lesssim E_R(N)/E_D(N=0) \lesssim 35\%$ in Fig. 1(c)] the computed desorption rates actually resemble the peak shape always observed for alkali/transition metal systems^{3,5-7,9,10,13} as it will be discussed in detail in the next section.

B. Comparison with experimental results and discussion

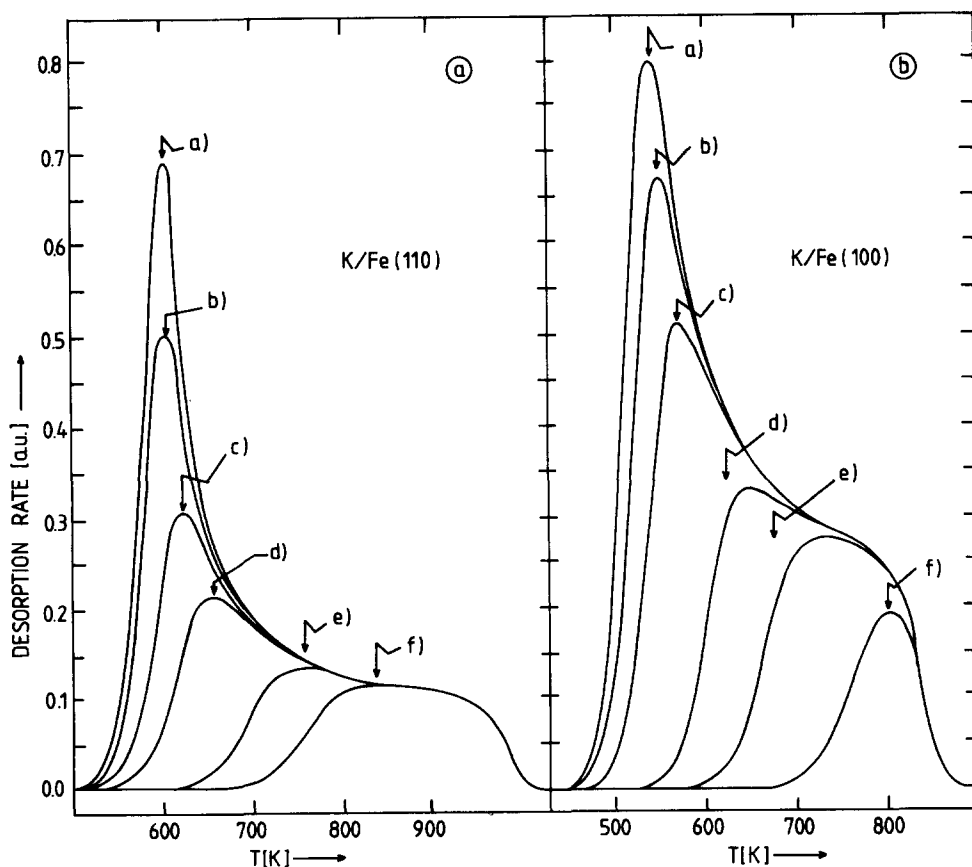


FIG. 2. Desorption rates of K adsorbed on Fe for various coverages. (a) K/Fe(110). $\alpha = 11.8 \text{ \AA}^3$, $P(N=0) = 8.5 \text{ D}$, $E_D(N=0) = 61.0 \text{ kcal/mol}$ and $\nu_0 = 10^{13} \text{ s}^{-1}$. The coverages $\{N \times 10^{-14} \text{ cm}^{-2}\}$ are: (a) 4.5, (b) 4.1, (c) 3.3, (d) 2.7, (e) 1.75, and (f) 1.25. (b) K/Fe(100). $\alpha = 11.0 \text{ \AA}^3$, $P(N=0) = 7.5 \text{ D}$, $E_D(N=0) = 52.0 \text{ kcal/mol}$, and $\nu_0 = 10^{13} \text{ s}^{-1}$. The coverages $\{N \times 10^{-14} \text{ cm}^{-2}\}$ are (a) 3.55, (b) 3.25, (c) 2.75, (d) 1.8, (e) 1.2, and (f) 0.45. The arrows indicate the maximum desorption rate experimentally determined (Ref. 7) for the same initial surface concentration as the above listed for the corresponding system.

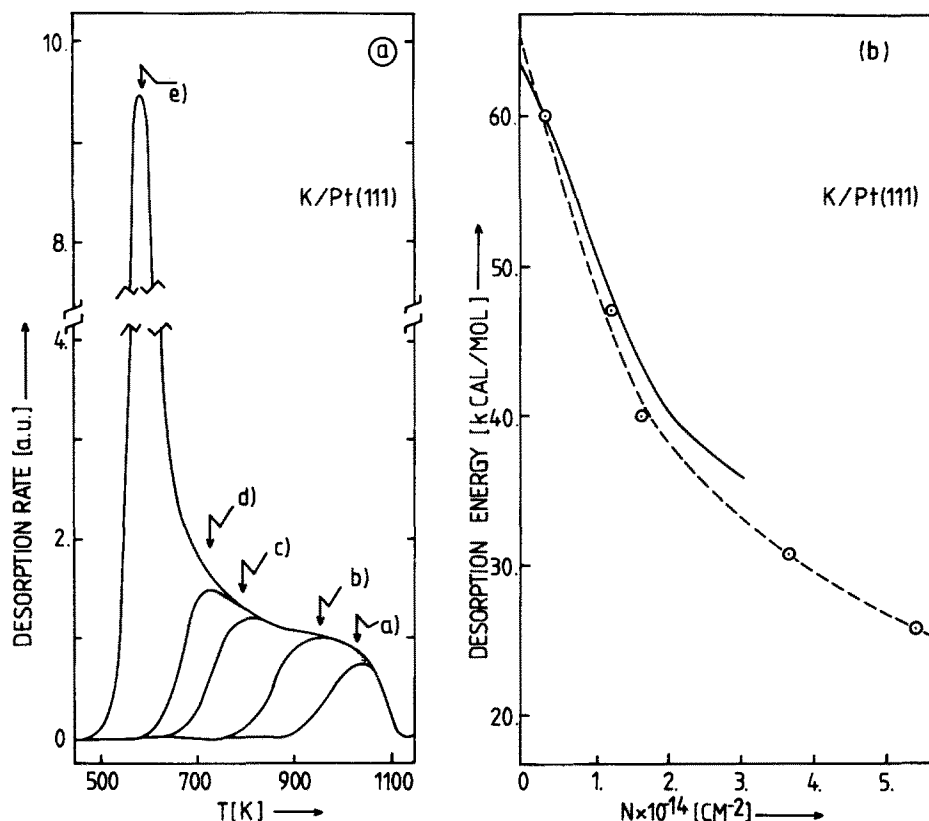


FIG. 3. (a) Desorption rates of K adsorbed on Pt(111) for various coverages calculated taking: $P(N=0) = 11.5 \text{ D}$, $\alpha = 17.2 \text{ \AA}^3$, and $E_D(N=0) = 63.7 \text{ kcal/mol}$. The coverages $\{N \times 10^{-14} \text{ cm}^{-2}\}$ are: (a) 0.32, (b) 0.76, (c) 1.3, (d) 1.62, and (e) 3.78. The arrows indicate the maximum desorption rate experimentally found (Refs. 9 and 10) for the same initial surface concentration as the above listed. (b) The coverage dependence of the activation energy of desorption. Full line: theoretical dependence evaluated replacing Eq. (7) in Eq. (2) and using the same values for the parameters as in (a). \odot Experimental values reported by Somorjai *et al.* (Refs. 9 and 10) (the dotted lines have been drawn to guide the eyes).

Desorption traces for K on different single crystal planes of Fe as well as on polycrystalline samples have been measured by Ertl *et al.*⁶⁻⁸ For the same systems, the K induced work function changes allow an alternative evaluation of $P(N=0)$ and α with the aid of the Topping model. Available published data have been summarized in Table I in order to be compared with the results of the present work.

Figures 2(a) and 2(b) show the computed TDS traces for K on Fe(110) and Fe(100). The spectra were evaluated assuming $\nu_0 = 10^{13} \text{ s}^{-1}$ ^{3,5,7,9,10} and the same surface concentrations of K reported in Ref. 7. In Fig. 2 the arrows indicate the temperature experimentally determined for the peak maxima (T_p). After selecting the best set of parameters (see Table I), the difference between experiment and theory lays within the error range for all the desorption peaks pointing out that the model gives an excellent description of the TDS of K from Fe.

Recently, Somorjai *et al.*^{9,10} reported desorption traces for K on Pt(111) showing a large shift in the desorption temperature ($T_p = 1033 \text{ K}$ for $N_0 = 0.33 \times 10^{14} \text{ cm}^{-2}$ and $T_p = 596 \text{ K}$ for $N_0 = 3.8 \times 10^{14} \text{ cm}^{-2}$) due to the dramatic decrease in the heat of desorption as a consequence of the repulsive interaction in the adlayer. Figure 3(a) shows the desorption traces for the system K/Pt(111) evaluated with the aid of Eq. (1). The calculations were made for the same surface coverage as the reported one for the experiments^{9,10} and the arrows indicate the measured position of the desorption peak^{9,10} in excellent agreement with the computed spectra. In order to perform the calculations a first order reaction rate has been assumed with a pre-exponential factor of $\nu_0 = 10^{13} \text{ s}^{-1}$ ^{3,5,7,9,10} Figure 3(b) shows the dependence of the heat of adsorption with coverage. The experimental data

were taken from the publications of Somorjai *et al.*^{9,10} The best fit to the TDS of Fig. 3(a) was attained for $E_D(N=0) = 63.7 \text{ kcal/mol}$ in good agreement with $E_D(N=0) = 65 \text{ kcal/mol}$ obtained extrapolating Somorjai's data^{9,10} in the limit for $N=0$. It is worth mentioning that for $E_D(N=0) = 63.7 \text{ kcal/mol}$, $P(N=0) = 11.5 \text{ D}$ (compared with 9.4 D , Ref. 26) and $\alpha = 17.2 \text{ \AA}^3$, an excellent agreement between experiment and theory has been reached evaluating both the TDS and the coverage dependence of the heat of desorption, as may be seen from Fig. 3.

TDS of Cs/W(110) have been reported by Desplat *et al.*⁵ The spectra are rather complex due to the simultaneous desorption of ionic and neutral species.⁵ Nevertheless, at low coverages, i.e., when the desorption of Cs ions is negligible,⁵ the TDS can be well fitted using the parameters listed in Table I and $\alpha = 24.5 \text{ \AA}^3$ which can be compared with $\alpha = 2.5 \text{ \AA}^3$ and $\alpha = 61 \text{ \AA}^3$ for ionic and neutral Cs, respectively.²⁸

As it follows from Table I the calculated activation energies of desorption in the limit of zero coverage are in good agreement with the reported data for the corresponding system. Except for the cases of Cs/W(110), Na/Ni(111), and Na/Ni(100), the values obtained for the dipole moment of the isolated adalkali are slightly higher than those estimated applying the Topping model to the nonlinear variation of the work function with coverage $\{\Delta\phi\}$. On the other hand, the effective polarizability of the adsorbed complex evaluated from TDS is smaller than that obtained with the Topping model for $\Delta\phi$. Since the guidelines followed in order to evaluate the depolarization effects on the adlayer of both the Topping model for $\Delta\phi$ and the present model for TDS are essentially the same and the values of $P(N=0)$ and α are in

both cases reasonable, it could be expected that the difference arises from the rough assumptions involved in the theory. It should also be kept in mind that in the case of $\Delta e\phi$ measurements, $P(N=0)$ is difficult to evaluate and very sensitive to the presence of errors in the coverage axis,¹⁹ while in the present case the selected parameters are capable of describing both the whole range of temperature of a given spectrum and the coverage dependence of a set of spectra. Nevertheless, it should be mentioned that for the interpretation of the TDS only the presence of long range through-space interactions between adsorbed dipoles is assumed and it is well known that electrostatic interactions are not the only source of adsorbate-adsorbate interactions.^{32,33} In fact, the contribution of indirect through-bond interactions (TBI)^{32,33} has not been considered since to our knowledge there are no calculations available for the system alkali/transition metals (see also Ref. 25). It should be interesting to estimate the short range behavior of the TBI since recently published experimental^{15,16} and theoretical^{18,25} results show unambiguously that the modification of the electronic properties of the substrate are strongly confined to the immediate vicinity of the adalkali. The contribution of the TBI, if repulsive, would cause a certain reduction in the magnitude of $P(N=0)$ necessary to obtain the best fit of the TDS data, and therefore a better agreement between the parameters evaluated from $\Delta e\phi$ and TDS models.

It should be mentioned that there exists a number of published TDS of alkali atoms which have not been analyzed for various reasons. In fact, the desorption of Na, K, and Cs from Ni single crystal surfaces³ has been performed with a nonlinear heating rate which renders the computation of the spectra and the comparison with the experimental results difficult. Nevertheless, the reported dependence of the activation energy of desorption for Na from Ni(111) and Ni(100) can be well described assuming $8 < \alpha < 10 \text{ \AA}^3$ and the parameters listed in Table I, which are in excellent agreement with the values published by Gerlach *et al.*³ For Na/Ni(111) the computed desorption maxima for $N_0 = 7 \times 10^{14} \text{ cm}^{-2}$ is $T_p = 525 \text{ K}$, also in agreement with the experimental data ($T = 540 \text{ K}$).³ In the case of K/Fe(111) two desorption states are discernible at low coverage.⁷ Modeling the simultaneous desorption from two adsorption sites, even neglecting the hopping probability between them, is beyond the aim of the present work. Finally, for the systems K/Ru(001)¹³ and Na/Ru(001)⁴³ the coverages with the respective alkali have not been determined unambiguously.

C. A simple method for assessing the coverage dependence of the activation energy of desorption

There are numerous methods for analyzing TDS (Refs. 34 and 35 and references therein). Most of them ignored the influence of surface coverage on the rate parameters and could be considered as refinements of the pioneering work of Redhead.³⁶ There are also few methods to assess the coverage dependence of the kinetic parameters (Refs. 37 and 38 and references therein) which generally need tedious experimental and mathematic work. The main advantage of the method proposed in this section is its simplicity.

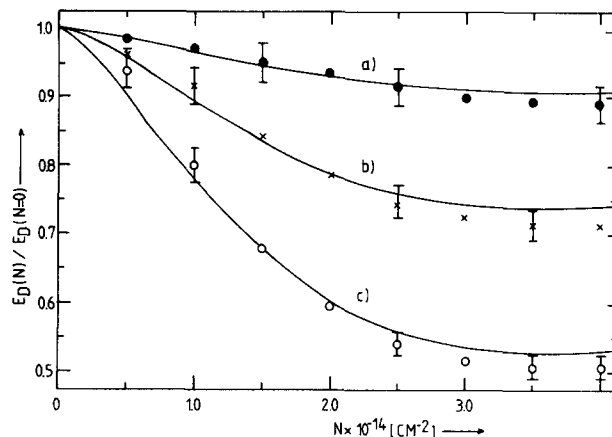


FIG. 4. The coverage dependence of the desorption energy relative to its value in the limit of zero coverage calculated for $\nu_0 = 10^{-13} \text{ s}^{-1}$ and the following values of the relevant parameters: (a) $E_D(N=0) = 50.0 \text{ kcal/mol}$, $P(N=0) = 4.0 \text{ D}$, and $\alpha = 12.0 \text{ \AA}^3$, (b) $E_D(N=0) = 60.0 \text{ kcal/mol}$, $P(N=0) = 8.0 \text{ D}$, and $\alpha = 14.5 \text{ \AA}^3$, (c) $E_D(N=0) = 65.0 \text{ kcal/mol}$, $P(N=0) = 12.0 \text{ D}$, and $\alpha = 17.0 \text{ \AA}^3$. The bars indicate an error of $\pm 3\%$ in the energy axis.

Redhead³⁶ has demonstrated that for a first order desorption without lateral interactions the relationship between the activation energy of desorption (E) and the temperature at which the desorption rate is maximum can be written as

$$E/RT_p = \ln\{\nu_0 T_p / \beta\} - 3.64, \quad (8)$$

where the employed symbols have been already defined.

Inspection of the desorption traces of alkali metals reveals a dramatic dependence of T_p on the coverage (see Figs. 2 and 3). Therefore it is possible to evaluate E for the different spectra using Eq. (8), but since this equation is only valid for noninteracting adsorbates there is no *a priori* relationship between E and the coverage. The results of a systematic study, which are summarized in Fig. 4 allow us to establish the following empirical relationship: within an error of $\sim \pm 3\%$, a plot of E vs the initial coverage (N_0) of the corresponding desorption spectrum, gives the correct dependence of the activation energy of desorption with coverage. For $N_0 > 4 \times 10^{14} \text{ cm}^{-2}$ [$\theta > \frac{3}{4}$ of a monolayer (ML) for most cases] and the largest repulsion energy [case (c) in Fig. 4] the error increases, being $\sim \pm 10\%$ for $N_0 = 5.4 \times 10^{14} \text{ cm}^{-2}$ (1 ML). In practice, the intrinsic error of the method must be added to the errors involved in the determination of T_p and N_0 . The overall error could be roughly estimated to be $\sim \pm 10\%$ – 15% , as may be expected in most methods for the determination of kinetic parameters from TDS.³⁹

No attempt has been made in order to strictly prove the proposed method, which is essentially empiric, by means of an appropriate mathematic treatment. Nevertheless the method can be qualitatively understood on the basis of the following arguments: (i) for low coverages the repulsive interaction is small because of the large average distance between neighboring dipoles. Therefore the first order reaction peaks are only slightly distorted and Eq. (8) yields to a good approximation the value of E . Furthermore, since the coverage at T_p is $N_p = N_0/e$ ($e = 2.718$ is the Euler constant),³⁶ the assignment of E to $N_0 > N_p$ causes the displacement of the points towards higher coverages and it is equiva-

lent to a slight overestimation of the actual desorption energy at N_p (see Fig. 4 for $N_0 < 1 \times 10^{14} \text{ cm}^{-2}$). (ii) At higher coverages the desorption maximum is sharp (see Figs. 2 and 3). Consequently $N_p \approx N_0$ and the assignment of E to N_0 is appropriate as may be seen in Fig. 4.

Summing up, the proposed empirical relationship holds for the wide range of interaction energies $[E_D(N)/E_D(N=0) \lesssim 0.5]$ which is characteristic for the alkali/transition metal systems. The method gives a quick and excellent approach of $E_D(N)$ which could eventually be employed in a more refined curve fitting as described in the previous sections.

III. THE EFFECT OF COADSORBED OXYGEN ON THE THERMAL DESORPTION ALKALI ATOMS

A. Brief description of the model

Model experiments dealing with the adsorption of alkali atoms on well characterized transition metal surfaces show that at the working temperature for a real catalytic process the alkali adlayer should be slowly lost by desorption with a substantial decrease in the promotor effect (see for instance Fig. 2 and compare with the working temperature of ammonia synthesis catalysts, i.e., 700 K).¹⁰ On the other hand, it is well known that coadsorbed oxygen thermally stabilizes the alkali adlayer,^{6,10} playing an important role in the long-time catalytic activity. It is worth mentioning that under actual catalytic conditions the alkali promotor is believed to be present as surface oxide^{27,40} although the exact stoichiometry of the compound is under debate.^{6,10,11}

As discussed in the previous sections, the alkali induced work function changes evidenced that the adatoms have the positive end of their electrical dipole pointing away from the surface.^{1,3-7,13,16,19,22} The opposite situation is observed after adsorbing oxygen atoms.^{6,29,41}

When both alkali and oxygen atoms approach each other on the surface, the electrical field originating from the dipole moment of each species increases that of the other and vice versa.²⁹ The strength of the mutual interactions depends on the magnitude of the involved dipole moments, the polarizabilities of the adatoms and their relative distances.²⁹ This interaction is evidenced in AES,⁶ TDS,^{6,10} work function^{6,11} measurements, and LEED patterns.¹⁰

In order to evaluate the repulsion energy between the adalkali in the presence of oxygen atoms, a generalization of Eq. (6) is necessary. In fact, for M different species, each of them having a concentration of N_i adparticles per unit surface area, polarizability α_i , and dipole moment $P_i(N_i)$, Eq. (6) becomes²⁹

$$P_j(N_j) = P_j(N_j = 0) + 9\alpha_j \sum_{\substack{i=1 \\ i \neq j}}^M P_i(N_i) N_i^{3/2}. \quad (9)$$

This system of M equations with M unknowns [i.e., $P_j(N_j)$] has to be solved for various coverages and must be handled according to the experimental conditions with concomitantly introduced additional assumptions as suggested by each particular case, if necessary.²⁹ For instance, if the concentrations of adalkali $\{N_A\}$ and oxygen $\{N_{ox}\}$ are different it could reasonably be supposed the existence on the

surface of the following species: (i) isolated adalkalis, (ii) isolated oxygen atoms, and (iii) various configurations of alkali-oxygen clusters. In order to make the computation of the desorption rate more treatable it has been assumed that (i) $N_A = N_{ox}$ and (ii) each oxygen atom is attached to an alkali adatom. These are realistic assumptions since: (i) the formation of alkali-oxygen pairs adsorbed on transition metal surfaces has been previously reported,^{6,29} (ii) if $N_A > N_{ox}$, TDS traces show that isolated alkali atoms desorb at lower temperatures than those stabilized with oxygen,⁶ (iii) if $N_{ox} > N_A$, it should be taken into consideration that the dipole moment of isolated oxygen adatoms [$P_{ox}(N_{ox} = 0) = 0.26 \text{ D}$ for O/Fe(110), Ref. 41] is considerably lower than the corresponding one for the adalkali [$P_A(N_A = 0) = 6.5 \text{ D}$ for K/Fe(110), see Table I]. For this reason and because of the larger average distance between isolated oxygen and alkali atoms (comparing with the dimer) the contribution to the attractive energy should be negligible.

Under the above discussed assumptions, the solution of the set of Eqs. (9) is

$$P_A(N_A) = [\gamma P_A(N_A = 0) + \alpha_A \delta P_{ox}(N_{ox} = 0)]/D, \quad (10a)$$

$$P_{ox}(N_{ox}) = [\Omega P_{ox}(N_{ox} = 0) + \alpha_{ox} \delta P_A(N_A = 0)]/D, \quad (10b)$$

where for $N_A = N_{ox} = N$,

$$\gamma = 1 + 9\alpha_{ox} N^{3/2}, \quad (11a)$$

$$\Omega = 1 + 9\alpha_A N^{3/2}, \quad (11b)$$

$$\delta = 9N^{3/2} + r_{AO}^{-3}, \quad (11c)$$

$$D = \gamma\Omega - \alpha_A \alpha_{ox} \delta^2, \quad (11d)$$

where r_{AO} is the alkali-oxygen distance in the dimer.

The depolarization field acting on each adalkali is given by

$$\epsilon_d = \epsilon_{d1} + \epsilon_{d2} + \epsilon_{d3}, \quad (12)$$

where

$$\epsilon_{d1} = -9P_A(N_A)N_A^{3/2} \quad (13a)$$

and

$$\epsilon_{d2} = 9P_{ox}(N_{ox})N_{ox}^{3/2} \quad (13b)$$

are, respectively, the field of the surrounding adalkalis and oxygen atoms, and

$$\epsilon_{d3} = P_{ox}(N_{ox}) \cdot r_{AO}^{-3} \quad (13c)$$

is the field of the adjacent oxygen atom in the dimer. Therefore, in the case of coadsorption the repulsion energy given by

$$E_R(N) = -P_A(N_A) \cdot \epsilon_d(N_A) \quad (14)$$

becomes

$$E_R = 9[P_A(N_A)]^2 N_A^{3/2} - \{9N_{ox}^{3/2} + r_{AO}^{-3}\} \cdot P_{ox}(N_{ox}) \cdot P_A(N_A) \quad (15)$$

which should be evaluated using Eq. (9) and then inserted into Eq. (2) in order to compute the activation energy of desorption.

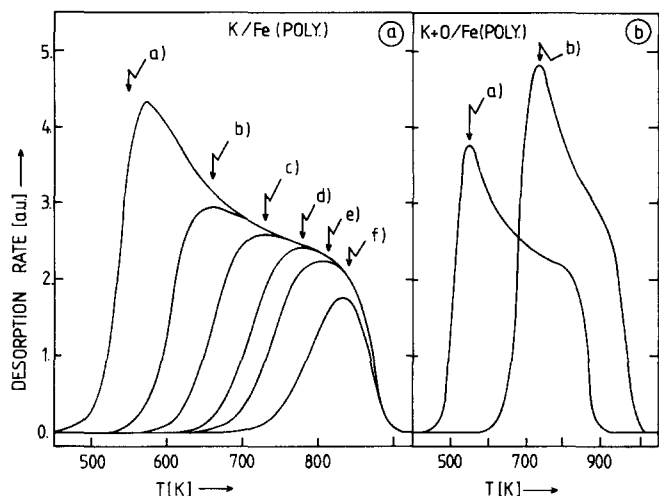


FIG. 5. (a) Thermal desorption traces of K adsorbed on Fe polycrystalline for various coverages calculated taking: P_A ($N_A = 0$) = 8.1 D, $\alpha_A = 11.3 \text{ \AA}^3$, and E_D ($N_A = 0$) = 54 kcal/mol. The coverages $\{N_A \times 10^{-14} \text{ cm}^{-2}\}$ are: (a) 2.58, (b) 1.75, (c) 1.30, (d) 0.95, (e) 0.75, and (f) 0.42. (b) The effect of coadsorbed oxygen on the desorption of K from Fe polycrystalline. (a) K/Fe calculated using the same parameters as in (a) for $N_A = 2.45 \times 10^{14} \text{ cm}^{-2}$. (b) K + O/Fe, evaluated using P_{Ox} ($N_{Ox} = 0$) = 1.2 D, $\alpha_{Ox} = 6.1 \text{ \AA}^3$ and $r_{AO} = 2.89 \text{ \AA}$, for $N_A = 2.61 \times 10^{14} \text{ cm}^{-2}$. The arrows indicate the maximum desorption rate experimentally found (Ref. 6) for the same initial surface concentration as the above indicated.

B. Comparison with experimental data and discussion

Figure 5(a) shows the computed TDS for K adsorbed on polycrystalline Fe at various surface coverages. The arrows indicate the peak position experimentally determined for the same coverage,⁶ in excellent agreement with the model. The effect of coadsorbed oxygen has been evaluated on the base of the parameters α_A and P_A ($N_A = 0$) obtained for the best fit in Fig. 5(a) (see also Table I). Figure 5(b) shows, for approximately the same initial coverage with the alkali, the computed desorption traces for both the K/Fe (poly) and K + O/Fe (poly) systems. Experimentally the peak of K shifts from 550 to 737 K [see the arrows in Fig. 5(b)] due to the presence of coadsorbed oxygen. This dramatic change in peak position can be well described by the proposed model assuming $\alpha_{Ox} = 6.1 \text{ \AA}^3$ and P_{Ox} ($N_{Ox} = 0$) = 1.2 D. Pirug *et al.*⁴¹ have reported P_{Ox} ($N_{Ox} = 0$) = 0.26 D for the dipole moment of chemisorbed oxygen on Fe(110). Moreover, the values P_{Ox} ($N_{Ox} = 0$) = 0.26 D and $\alpha_{Ox} = 2.7 \text{ \AA}^3$ have previously been employed to describe the work function changes induced for the coadsorption of K and oxygen on Fe surfaces.²⁹

The distance between oxygen and K atoms in a dimer has been taken as $r_{AO} = 2.89 \text{ \AA}$.²⁹ This value is comparable to the sum of the average ionic radii for K^+ (1.33 \AA) and O^{2-} (1.4 \AA),⁴² and is in good agreement with the interatomic K–O distance on Pt(111) estimated in order to interpret LEED patterns.¹⁰

The TDS of K thermally stabilized by oxygen on Pt(111) has also been calculated. Using the polarizability and dipole moment obtained by fitting the system K/Pt(111) (see Table I), P_{Ox} ($N_{Ox} = 0$) = 1.2 D and $\alpha_{Ox} = 5.0 \text{ \AA}^3$ the computed desorption maximum of K ($T_p = 650 \text{ K}$) are shifted by 220 K toward higher temperatures due to the

presence of coadsorbed oxygen (for $N_A = 2.7 \times 10^{14} \text{ cm}^{-2}$) in agreement with the results of Somorjai *et al.*¹⁰ Our results also show that at 700 K the desorption rate of K in the system K + O/Pt(111) is negligible and consequently the concentration of the electronic promotor on the metallic surface at this temperature becomes threefold enhanced.

Preliminary results show that at constant temperature the desorption of alkali metals stabilized with oxygen is negligible for $T < 700 \text{ K}$ in good agreement with the previous results. This factor would be of importance under actual catalytic conditions.

It is worth mentioning that in spite of the rough assumptions involved, the model for coadsorbed dipoles satisfactorily describes the two more striking features of the alkali + oxygen/transition metal systems, i.e., the enhancement of the electron emission from the surface²⁹ and the thermal stabilization of the alkali adlayer.

IV. CONCLUSIONS

A model, capable of explaining the TDS of alkali atoms from transition metal surfaces, based on the calculation of the repulsion energy between coplanar dipoles has been developed and discussed. The model describes successfully the experimentally found coverage dependence of both peak position and activation energy of desorption.

The presented results also show that the main features of the studied systems are a consequence of dipolar forces within the adlayer, suggesting that indirect through-bond interactions should contribute to a much lesser extent.

A systematic study covering a wide range of interaction energies enables us to propose a simple and accurate method of assessing the coverage dependence of the desorption energy.

A generalization of the proposed model is also developed in order to understand the coadsorption of electropositive and electronegative species. The results reveal that the presence of oxygen adatoms substantially decreases the repulsion energy affecting the adalkalis. Consequently the alkali adlayer becomes stabilized by coadsorbed oxygen in agreement with available experimental data.

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