

Regular article

Theoretical study of the adsorption of oxygen on a Cu(100) surface and the coadsorption with alkali atoms

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Abstract. We performed a theoretical study of the adsorption of oxygen on a cluster model of the Cu(100) surface and also the surface coadsorbed with lithium and potassium atoms. The study showed that alkali coadsorption facilitates in a significant way the process of molecular adsorption, whereas the adsorption of atomic oxygen is only slightly modified. The alkali atoms on the copper surface produce an increase in the charge transfer toward the oxygen molecule, favoring the oxygen dissociation. The effect is greater for the potassium coadsorption. In addition, we found that the potassium coadsorption favored the dissociation and recombination processes by about 60 and 15%, respectively. In turn, the lithium coadsorption favored only the recombination process by about 50%. These results could be an important aspect for catalytic processes.

Keywords: Oxygen – Alkali – Adsorption – Copper – Surface

1 Introduction

The study of oxygen adsorption on transition-metal surfaces is important for the understanding of heterogeneous catalysis and corrosion [1, 2, 3, 4, 5, 6, 7]; hence, oxygen–metal surface systems have been studied intensively [7, 8]. It has been found that, in general, molecular oxygen directly dissociates on the surface or does so after adsorption. The process is characterized by charge transfer from the surface to the oxygen atoms and the dissociation occurs through an activation process [6, 8]. The presence of alkali metals, previously adsorbed on

the surface, helps the dissociation of molecular oxygen. In the presence of alkali metals the charge transfer is more effective in lowering the activation energy [7, 9]. In the specific case of copper, the adsorption of molecular oxygen is found on the three main surfaces, i.e., (100), (110) and (111). In all processes the adsorption is exothermic and an activation energy is found [4, 5, 10]. Using X-ray photoelectron spectroscopy and UV photoelectron spectroscopy techniques the molecular oxygen adsorption on the copper surfaces at 100 K has been observed, whereas atomic oxygen has been observed only over 300 K [11, 12]. In addition, the presence of alkali metals on copper surfaces facilitates the dissociation of molecular oxygen; the increase in the velocity of the reaction is estimated to be 4 to 6 times [7, 9].

In this work, we present an electronic structure study of the changes in the adsorption of oxygen on Cu(100) in the presence of lithium or potassium atoms previously adsorbed on the surface. Our interest is to characterize the electronic structure of the system for both processes (molecular and atomic adsorption) and to study the way alkali metals modify these processes. The copper surface was modeled by using a cluster approach and density functional methods were used for the electronic structure calculations.

2 Methodology

2.1 Cluster model

The adsorbate–copper surface interaction has been successfully described by means of clusters models [13, 14, 15]. Since the work of Bagus and Illas [16], who succeeded in explaining the main features of the oxygen–copper surface interaction using a cluster of five atoms, different clusters with a variable number of atoms have been used [14, 15]. In this work, the Cu(100) surface was represented by a cluster of 14 atoms: nine Cu atoms in the first layer, four Cu atoms in the second layer and one Cu atom in the third layer. The cluster can be represented as Cu(9:4:1) (Fig. 1a). A Cu–Cu distance of 2.56 Å

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(distance in the bulk solid) was used to build up the cluster. The oxygen chemisorption on a copper surface is a local process. There is evidence that the process is determined by local interactions [17, 18]; therefore, the size of the cluster should not be so critical as long as the local site of the adsorption is well represented.

It has been proposed [13, 15] that the oxygen molecule approaches parallel to the surface; therefore, in this work the oxygen molecule was positioned parallel to the surface with the oxygen atoms pointing

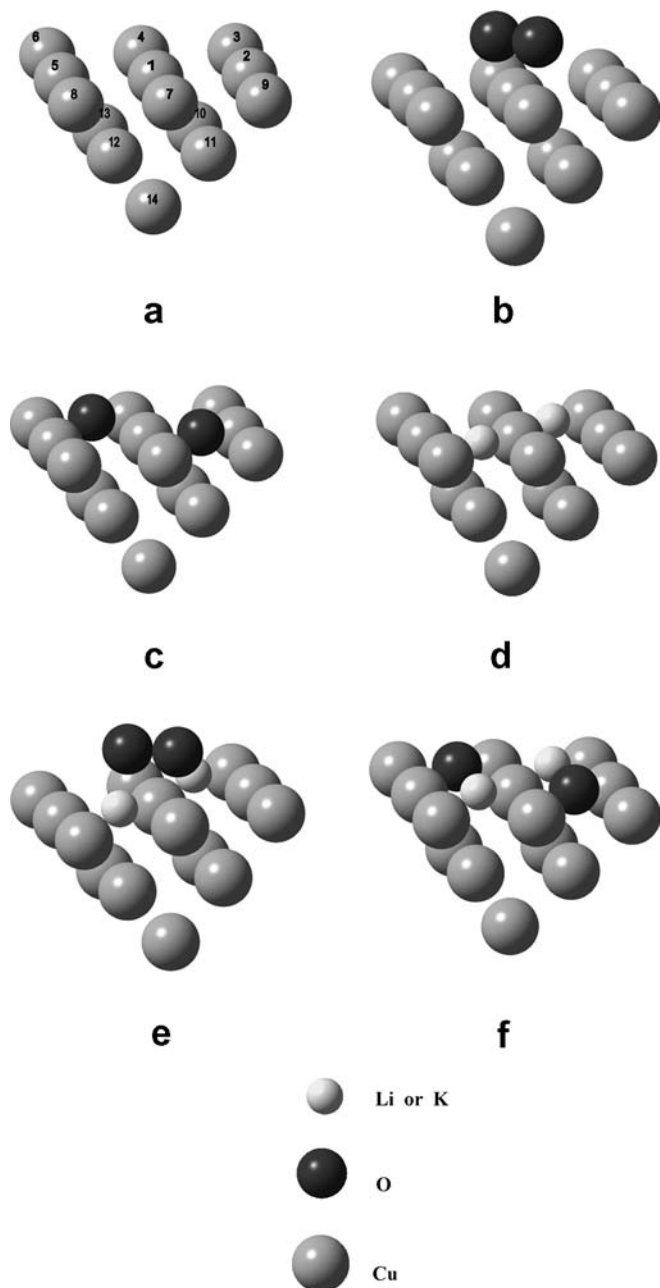


Fig. 1a–f. Cluster models. **a** Clean copper surface. **b** Adsorption of oxygen molecule on a clean copper surface. **c** Adsorption of atomic oxygen on a copper surface. **d** Alkali adsorption on the clean copper surface. **e** Oxygen molecule coadsorbed with alkali atoms on the copper surface. **f** Atomic oxygen coadsorbed with alkali atoms on the copper surface

toward a fourfold site and the O–O bond region over a copper atom in a top position (Fig. 1b). Keeping the copper cluster structure rigid the distance of the molecule to the surface and the O–O distance were optimized simultaneously. For the molecular adsorption a bridge position is also reasonable and is expected to occur; however, the adsorption at a bridge position is not followed by the dissociative chemisorption which is also of interest in this work. To describe the adsorption of atomic oxygen, two atoms were positioned into fourfold sites and the distance to the surface was optimized [$R(\text{O}-\text{Cu}_{14}) = 0.8 \text{ \AA}$, Fig. 1c]. This result is in good agreement with the experimental data, which yield a distance of $0.8(3) \text{ \AA}$ [19]. To simulate the coadsorption of alkali atoms, two alkali atoms were positioned in a fourfold site and the distance to the surface was optimized (Fig. 1d–f). The results are 1.7 and 2.8 \AA for lithium and potassium, respectively. These values are in good agreement with experimental data [20]. For lithium the effects of the rate of coverage over the surface are not known; however, for the case of potassium coadsorption there are some results indicating that a high coverage is more favorable [9, 21, 22].

2.2 Methods of calculation

The Stuttgart pseudopotential for the copper atom was used [23]. It consists of ten core electrons and 19 active valence electrons. The recommended $8s7p6d/[6s5p3d]$ basis set [23] was carefully shortened to a $7s6p5d/[5s4p2d]$ basis set in order to make the calculations feasible. Test calculations using the original basis set do not show any significant change in the results. For the potassium atom the Stuttgart pseudopotential and the corresponding basis set were used; it consists of ten core electrons and nine active valence electrons [24]. The natural bond order (NBO) population analysis [25, 26, 27] was used for the discussion of the results. For oxygen and lithium atoms all electrons were explicitly considered and a standard $6-311+G^*$ basis set [28, 29] was used. The basis sets associated with the Stuttgart pseudopotentials were constructed to be used in conjunction with all-electron basis sets, avoiding as much as possible unbalanced situations. The Kohn–Sham equations were solved using the B3LYP [29, 30, 31, 32] exchange–correlation functional, which is of the hybrid type. It consists of a careful mixing of Hartree–Fock exchange, calculated with the Kohn–Sham orbitals, and the B88 exchange functional [31] plus the LYP correlation functional [33]. All the calculations were performed using the G98 program [30].

The binding energy of the adsorption process was calculated as

$$E_b = E[\text{Cu}_{14}\text{O}_2(\text{m})] - E(\text{Cu}_{14}) - E(\text{O}_2) \quad (1)$$

for the clean surface and as

$$E_b = E[X_2\text{Cu}_{14}\text{O}_2(\text{m})] - E(X_2\text{Cu}_{14}) - E(\text{O}_2); \quad X = \text{Li, K} \quad (2)$$

for the coadsorbed system. For the adsorption of atomic oxygen the binding energy was calculated as

$$E_b = \frac{1}{2} \{E[\text{Cu}_{14}\text{O}_2(\text{a})] - E(\text{Cu}_{14}) - 2E(\text{O})\} \quad (3)$$

for the clean surface and as

$$E_b = \frac{1}{2} \{E[X_2\text{Cu}_{14}\text{O}_2(\text{a})] - E(X_2\text{Cu}_{14}) - 2E(\text{O})\}; \quad X = \text{Li, K} \quad (4)$$

for the coadsorbed system. Here, $\text{Cu}_{14}\text{O}_2(\text{m})$ and $X_2\text{Cu}_{14}\text{O}_2(\text{m})$ represent the oxygen molecule adsorbed on a clean surface and coadsorbed with alkali atoms, respectively. $\text{Cu}_{14}\text{O}_2(\text{a})$ and $X_2\text{Cu}_{14}\text{O}_2(\text{a})$ represent oxygen atoms on fourfold sites on a clean surface and coadsorbed with alkali atoms, respectively.

3 Results and discussion

The calculated ionization energies and electroaffinities for the atomic species lithium, potassium, oxygen and copper, and also the Cu_{14} cluster are compared with experimental values of the atomic species and the copper metal, respectively in Table 1. This gives a measure of the reliability of our calculations. One can see that the ionization potentials are systematically overestimated and that the electronaffinities are underestimated with the exception of atomic oxygen. The Cu_{14} cluster as a model of the bulk performs well in the ionization process but, of course, is not able to describe the negatively charged system. This failure will not be of concern here because in this study the copper surface lost charge. As a further test of the reliability of our calculations we present in Table 2 the bond lengths and bonding energies for the diatomic molecules O_2 , Cu_2 , CuO , CuLi and CuK , and also for the cluster Cu_{14}O in comparison with the experimental values for the diatomic molecules and the experimental values of the solid for the cluster. We can see that the agreement for the bond lengths is excellent. The bond energies are systematically overestimated by approximately 6 kcal/mol; hence, in general, one can expect a systematic error in the energy differences of the same order, i.e., of around 6 kcal/mol.

Energies and geometrical parameters for the molecular and atomic oxygen adsorption on a clean $\text{Cu}(100)$ surface and coadsorbed with alkali atoms are displayed

Table 1. Ionization potentials (*IP*) and electron affinities (*EA*). Theoretical versus experimental values

	IP (kcal/mol) Theory/Exp	EA (kcal/mol) Theory/Exp
Li	129.6/124.3 ^a	12.9/14.3 ^b
K	103.7/100.1 ^a	10.4/11.6 ^b
O	325.8/314.1 ^a	37.1/33.7 ^b
Cu	179.9/178.3 ^a	18.2/28.4 ^b
Cu_{14}	126.1/113.7 ^c	43.4/113.7 ^c

^a Ref. [43]

^b Ref. [44]

^c Ref. [42]

in Table 3. In the adsorption of molecular oxygen on a clean surface the energy gain is 2.8 kcal/mol. This value is lower than the possible error of our calculations. However, experimentally, molecular adsorption has only been determined under 100 K [35, 36]. It has not been possible to measure the heat of adsorption, although there is evidence that it is small [35, 36]. The molecule is parallel to the surface at the top position and the O–O distance is 1.32 Å; hence, the bond is longer than that of the molecule in the gas phase (1.21 Å). The presence of alkali atoms on the surface changes dramatically the energetics of the adsorption of molecular oxygen. The Li atoms favor the adsorption process by about 60 kcal/mol, giving a total energy gain of 64.1 kcal/mol and an O–O distance of 1.54 Å. For the potassium coadsorption the situation is similar, but favoring the adsorption process only by about 32 kcal/mol. The O–O distance is in this case 1.55 Å, similar to what one finds for the lithium coadsorption. On the other hand, atomic oxygen adsorption is slightly modified by the presence of lithium atoms on the surface. The adsorption energy per oxygen atom is 94.1 kcal/mol for the clean surface and 97.0 and 108.4 kcal/mol for Li and K coadsorption, respectively. The oxygen atoms are at a fourfold position 0.8 Å from the surface. This is in good agreement with the experimental value of 0.8(3) Å obtained by the surface-extended X-ray absorption fine structure technique [19]. From our calculations the same distance in the

Table 2. Equilibrium distances R_e and dissociation energies D_e . Theoretical versus experimental values

	R_e (Å) Theory/Exp	D_e (kcal/mol) Theory/Exp
O_2	1.206/1.207 ^a	119.7/117.1 ^a
Cu_2	2.19/2.22 ^a	55.3/47.3 ^a
CuO	1.73/1.73 ^b	72.4/65.3 ± 3.5 ^b
CuLi	2.19/2.26 ^c	48.7/43.7 ^c
CuK	2.98/2.99 ^d	30.2/31.1 ^d
Cu_{14}O	0.8/0.8(3) ^e	94.5/99.2 ^f

^a Ref. [45]

^b Ref. [46]

^c Ref. [47]

^d Ref. [48]

^e Ref. [17]

^f Ref. [49]

Table 3. Relative energies (Kcal/mol) and equilibrium distances (Å) in. R_h is the equilibrium distance between a copper atom on a top site and the molecular oxygen bond. R_O is the distance between the plane formed for four copper atoms at the first layer and atomic oxygen

	ΔE	R_h	R_O	$R(\text{O–O})$
Molecular adsorption				
O_2	–2.8	2.10	–	1.32
O_2 –Li coadsorption	–64.1	1.98	–	1.54
O_2 –K coadsorption	–31.8	1.75	–	1.55
Atomic adsorption				
O	–94.1	–	0.80	–
O–Li coadsorption	–97.0	–	1.10	–
O–K coadsorption	–108.4	–	1.21	–

presence of the lithium or potassium atoms is 1.10 and 1.21 Å, respectively. The adsorption of alkali atoms induces a lowering of the work function by 0.37 and 0.96 eV for Li and K, respectively. These shifts compare well with the available experimental data [36, 37, 38, 39, 40, 41]. The value of the work function is also in good agreement with previous calculations [14]. The decrease of the work function means that the adsorption of alkali atoms produces a charge transfer to the surface favoring the coadsorption of electrophilic species. It is possible to rationalize this result by means of the NBO population analysis which is shown in Table 4. The numbering of the copper atoms is the same as in Fig. 1. Hence, copper atom 1 is at the center of the cluster and it is the only one with the coordination number of a copper surface. On the clean surface this atom is clearly negatively charged and the presence of alkali atoms on the surface augments the negative charge on it and also on the neighboring copper atoms. Hence, the oxygen molecule, positioned with the bond just on top of this atom takes charge from the surface which should go to the half-filled antibonding π^* molecular orbital, explaining that the molecular bonding is weaker and the bond longer. From Table 4, one can see that the NBO analysis yields a negative charge of approximately $0.45e$ on each oxygen atom in the case of a clean surface and about twice as much charge with alkali coadsorbed, $0.88e$ for Li and $0.95e$ for K. An interesting correlation between the oxygen charge for the adsorption of an oxygen molecule and the charge of the alkali atoms can be established (Fig. 2). The charge transferred for alkali atoms is directly proportional to the charge accepted for oxygen atoms. In the atomic oxygen adsorption the situation is different. Here, the charge transfer to the oxygen atom is

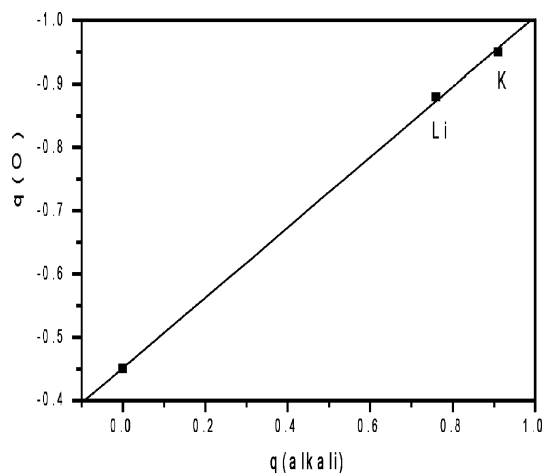


Fig. 2. Oxygen charge in an oxygen molecule, $q(O)$, versus alkali charge, $q(\text{alkali})$, in the adsorption process

almost complete on the clean surface. The NBO analysis yields a charge of $1.65e$ on each oxygen atom. In the presence of alkali atoms this value augments to $1.74e$ for Li and $1.78e$ for K coadsorptions, which do not represent a significant change. It is interesting to note that experimentally, at low coverage, a peroxo type of oxygen (O_2^-) at bridge positions is found [6], which is in accord with our model calculations.

Because of the practical limitations to calculate the transition state of the total process, i.e., molecular adsorption, suitable for the dissociation to finish in the atomic adsorption, a possible path has been calculated. It consists of a linear path going from the molecular adsorption equilibrium geometry to the atomic one. On

Table 4. Natural bond order population analysis. Values correspond to natural charge in a specific atom. Cu_{14} represents the copper cluster. Cu_{14}/O_2 represents the oxygen molecule adsorbed on the copper cluster. $Cu_{14}/O(2)$ represents the oxygen atoms adsorbed on the copper cluster. $Cu_{14}/X(2)$ ($X = \text{Li, K}$) represents

alkali atoms adsorbed on the copper cluster. $Cu_{14}/X(2)/O_2$ ($X = \text{Li, K}$) represents alkali atoms and an oxygen molecule coadsorbed on the copper cluster. $Cu_{14}/X(2)/O(2)$ ($X = \text{Li, K}$) represents alkali atoms and oxygen atoms coadsorbed on the copper cluster

Atom	Cu_{14}	Cu_{14}/O_2	$Cu_{14}/O(2)$	$Cu_{14}/Li(2)$	$Cu_{14}/K(2)$	$Cu_{14}/Li(2)/O_2$	$Cu_{14}/K(2)/O_2$	$Cu_{14}/Li(2)/O(2)$	$Cu_{14}/K(2)/O(2)$
1 Cu	-0.42	0.12	0.64	-0.62	-0.59	0.03	0.25	0.40	0.45
2 Cu	0.10	-0.04	0.48	-0.15	-0.15	-0.08	-0.07	0.04	0.05
3 Cu	0.04	0.12	0.27	0.06	0.01	0.10	0.01	0.42	0.41
4 Cu	-0.09	-0.04	0.48	-0.15	-0.15	-0.08	-0.07	0.04	0.05
5 Cu	-0.09	-0.04	0.48	-0.15	-0.15	-0.08	-0.07	0.04	0.05
6 Cu	0.04	0.11	0.02	-0.14	-0.22	-0.07	-0.13	-0.03	-0.06
7 Cu	-0.09	-0.04	0.48	-0.15	-0.15	-0.08	-0.07	0.04	0.05
8 Cu	0.04	0.12	0.27	0.06	0.01	0.10	0.01	0.42	0.41
9 Cu	0.04	0.11	0.02	-0.14	-0.22	-0.07	-0.13	-0.03	-0.06
10 Cu	0.16	0.12	-0.05	0.22	0.22	0.20	0.21	0.02	-0.01
11 Cu	0.16	0.17	0.08	-0.23	-0.20	0.05	0.01	0.24	0.19
12 Cu	0.16	0.12	-0.05	0.22	0.22	0.20	0.21	0.02	-0.01
13 Cu	0.16	0.17	0.08	-0.23	-0.20	0.05	0.01	0.24	0.19
14 Cu	-0.03	-0.10	0.11	0.24	0.22	-0.03	-0.09	0.00	-0.02
Li				0.57		0.76		0.83	
Li				0.57		0.76		0.83	
K					0.68		0.91		0.93
K					0.68		0.91		0.93
O		-0.45	-1.65			-0.88	-0.95	-1.74	-1.78
O		-0.45	-1.65			-0.88	-0.95	-1.74	-1.78

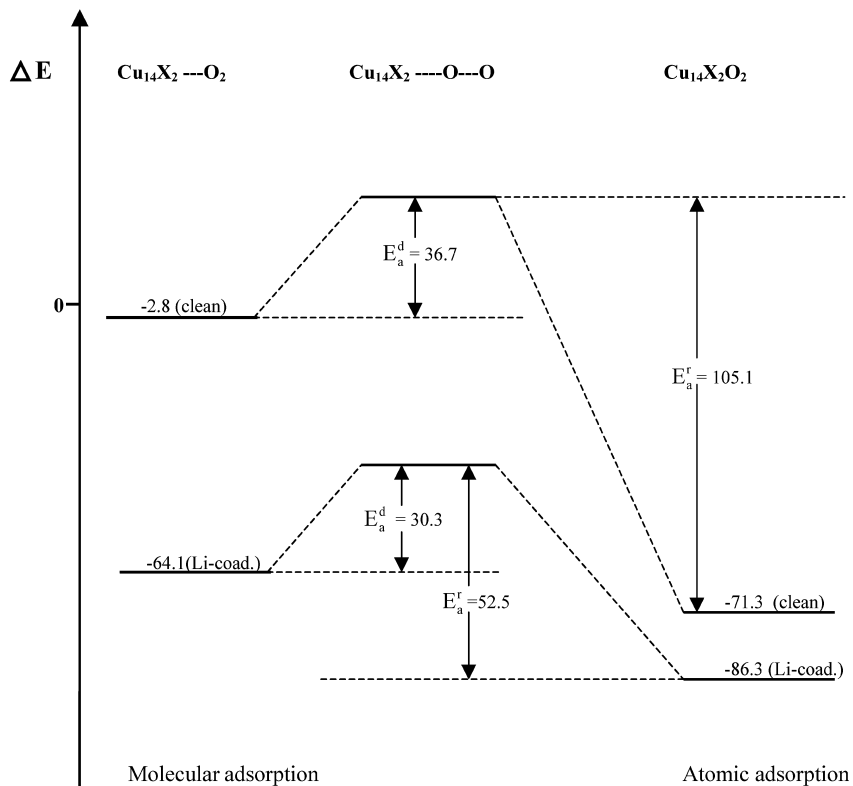
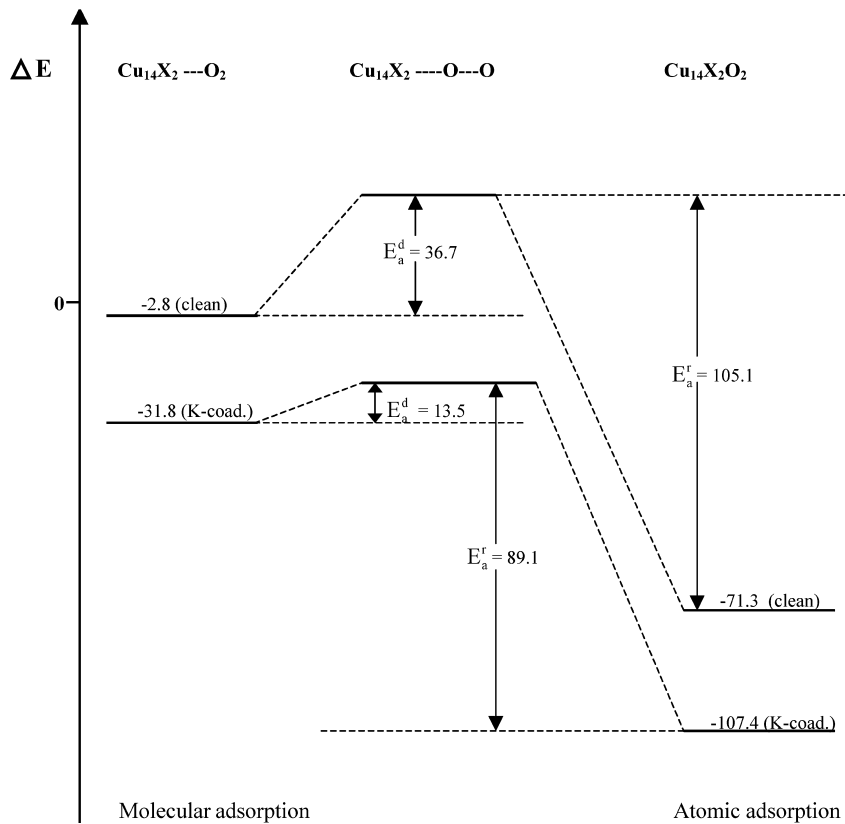
a**b**

Fig. 3a,b. Schematic representation of the energies of the adsorption processes. The energies are calculated taking as a reference the system $\text{O}_2 + \text{Cu}_{14}\text{X}_2$, where X represents the possibility of alkali coadsorption. E_a^d is the activation energy for the dissociation process, and E_a^r is the activation energy for the recombination process. **a** Lithium coadsorption. **b** Potassium coadsorption. Energies are given in Kilocalories per mole

this path, only the oxygen atoms are moved. The energy maximum on this path has been associated as a possible transition state for the dissociation process. To compare the total process we recalculated the binding energy for the full process as relative to the molecular oxygen system. So we have

$$E_b = E[\text{Cu}_{14}\text{O}_2(\text{a})] - E(\text{Cu}_{14}) - E(\text{O}_2) \quad (5)$$

for the clean surface and

$$E_b = E[X_2\text{Cu}_{14}\text{O}_2(\text{a})] - E(X_2\text{Cu}_{14}) - E(\text{O}_2); \quad X = \text{Li}, \text{K} \quad (6)$$

for the coadsorbed system. It is expected that the calculated activation energy would resemble in a qualitative way the activation energies which should be obtained from the true transition state. The results are shown in Fig. 3. One can see that for the direct process, dissociation of the oxygen molecule, the activation energy in the presence of Li atoms is about 6 kcal/mol lower than for the clean surface (Fig. 3a). The value is small and of the order of the inaccuracy of the calculations. Hence, it is evidence that the changes in the dissociation process are small. However, for the recombination process, formation of the oxygen molecule, the Li coadsorbed system has an activation energy about 52 kcal/mol lower than the clean surface. On the other hand, in the presence of potassium atoms the activation energy is about 23 kcal/mol lower than for the clean surface (Fig. 3b). So, for this case the presence of potassium atoms favors the dissociation of the oxygen molecule. In addition, for the recombination process the K coadsorbed system has an activation energy about 16 kcal/mol lower than the clean surface. The effect is smaller than what one finds for the Li coadsorbed system. These results explain further the significant increase in the catalytic activity of an oxygen molecule when the copper surface previously adsorbs alkali atoms. The energy differences are large enough to assume that the qualitative picture presented will not be changed by more-accurate calculations.

4 Conclusions

In the present work some processes for the interaction of an oxygen molecule with a copper surface have been analyzed. The results showed that the presence of alkali atoms on the surface facilitates in a significant way the process of molecular oxygen adsorption, whereas the atomic adsorption is only slightly modified by the presence of alkali atoms. This has been rationalized by means of a NBO population analysis which has shown an important charge transfer from copper surface to oxygen atoms. The presence of alkali atoms on the copper surface produces an increase of the charge transfer in the adsorption process, favoring the oxygen dissociation. Furthermore, on the Li coadsorbed system the recombination barrier decreases significantly by about 50%. On the other hand, on the K coadsorbed system the dissociation barrier decreases by about 60%. These results provide evidence for the different nature of

lithium and potassium atoms when they are adsorbed on the copper surface, an important aspect for the use of a specific alkali for a certain catalytic process.

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