THEORETICAL STUDY OF THE ADSORPTION OF OXYGEN ON SMALL BIMETALLIC K_mCu_n ($m, n \leq 4$ AND $m, n=1, 12$) CLUSTERS

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ABSTRACT

A theoretical study of the adsorption of molecular oxygen on small bimetallic K_mCu_n ($m, n \leq 4$ and $m, n=1,12$) clusters was carried out using density functional methods, and compared with the adsorption of O_2 on bimetallic Li_mCu_n ($m, n \leq 4$) clusters. The study of the O_2 - K_mCu_n system is important to understand the promotion effects of the alkali atoms on the copper surface participating in the catalytic processes. Adsorption energies ranging from 5.7 to 48.6 kcal/mol were found, which represented values slightly smaller than those calculated for the adsorption of O_2 on Li_mCu_n clusters in a previous study. However, the global reactivity towards O_2 was higher in K_mCu_n than in Li_mCu_n clusters.

Keywords: alkali-copper cluster, O_2 adsorption, quantum chemical calculations.

INTRODUCTION

The study of small metal clusters has received considerable attention on the theoretical as well as the experimental level due to their potential application in the catalytic processes and electronic materials [1-3]. Clusters containing as little as a few to several thousand atoms have been studied to determine the evolution of the bulk matter properties from atomic properties [4]. In addition, the basic properties of metal clusters are believed to be an important link in understanding the fundamental mechanism of catalysis and other chemical transformations [5,6]. Recently, the study of adsorption of gases on clusters of noble and transition metals was carried out [7-19]. The effect of catalytic promotion is an interesting, but unanswered question related to the properties of impurities, such as alkali atoms on metal surfaces. Thus, the study of bimetallic clusters is important as it could help clarify the properties of these impurities. Recently, a theoretical study concerning the adsorption of molecular oxygen on bimetallic lithium-copper clusters [20] was reported. The previous study demonstrated that the reactivity of O_2 on bimetallic clusters was higher than that for copper clusters. In addition, an adsorption energy about 30 to 68% greater in comparison to the Cu_nO_2 ($n \leq 8$) system was found in the $Li_mCu_nO_2$ system. The above mentioned result was fundamentally related to the lithium atoms in bimetallic clusters for increasing the charge transfer towards the O_2 molecule. The existence of a charge transfer was indicative of the chemisorptions' process.

Studies of surfaces demonstrate that lithium and potassium deposited on copper surfaces modify the surface properties, thereby presenting differences in the reactivity towards the adsorbates [21]. Thus, it is believed that the manner in which lithium and potassium interact with the copper surfaces is different, whereby the characteristics have not yet been solved completely. Consequently, the cluster study can help to elucidate these aspects. Thus, the aim of the present work is to study the adsorption of the molecular oxygen on small bimetallic K_mCu_n ($m, n \leq 4$) clusters using functional density methods, and comparing their properties with the adsorption of O_2 on Li_mCu_n clusters, as recently reported [20]. In addition, the $KCu_{12}O_2$ system is also analyzed to study the behavior of the adsorption of oxygen on a bigger bimetallic cluster.

METHODOLOGY AND COMPUTATIONAL DETAILS

Energy and electronic properties have been calculated by solving the Kohn-Sham equations in an atomic basis set formed by Gaussian functions. The calculations have been done using the B3LYP [22-25] exchange correlation functional, which is of the hybrid type. This consists of a careful mixing of the Hartree-Fock exchange, calculated with Kohn-Sham orbitals, and the B88 exchange functional [24] plus the LYP correlation functional [25]. The use of the B3LYP functional has been utilized in previous calculations with good agreement with the experimental data [17, 20]. The Stuttgart pseudopotential [26] with the corresponding basis set (8s7p6d) has been used for the copper atoms. The pseudopotential replaces the ten core electrons. Thus, nineteen valence electrons have been considered. A new Stuttgart pseudopotential [27] with the corresponding basis set (11s11p5d) has been used for the potassium

atoms. The pseudopotential replaces the ten core electrons. Thus, nine valence electrons have been considered. The D95+(d) basis set [28,29] has been used for the oxygen atom. The calculated bond length and bond energy for the gas phase O_2 were 1.22 Å and 120.4 kcal/mol, respectively, which was in good agreement with the experimental values of 1.21 Å and 120.6 kcal/mol, as reported previously [20]. The natural bond order (NBO) population analysis [30,31] was used for the discussion of the obtained results. Initial geometries of bimetallic K_mCu_n clusters were those optimized in a previous study [32]. The initial geometry for the KCu_{12} cluster was determined in the present work and is shown in Fig. 1. The interaction of molecular oxygen with the bimetallic clusters was fully optimized without symmetry restrictions in different adsorption sites (top, bridge and threefold hollow) and orientations on the bimetallic cluster. All the calculations were done of the unrestricted type using the Gaussian 98 package [33].

The binding energy for the $K_mCu_nO_2$ system was calculated as:

$$E_b = E(K_mCu_nO_2) - mE(K) - nE(Cu) - 2E(O); \quad n, m \leq 1-4 \text{ and } m, n=1, 12 \quad (1)$$

and the adsorption energy for the optimum process was calculated as:

$$E_{ad} = E(K_mCu_nO_2) - E(K_mCu_n) - E(O_2); \quad n, m \leq 1-4 \text{ and } m, n=1, 12 \quad (2).$$

$E(K_mCu_nO_2)$, $E(K_mCu_n)$, $E(O)$, $E(K)$, $E(Cu)$ and $E(O_2)$ being the energies of O_2 -bimetallic cluster, bare bimetallic cluster, oxygen atom, potassium atom, copper atom and molecular oxygen, respectively. Equations (1) and (2) are similar to the ones used to calculate the binding and adsorption energies in the adsorption of molecular oxygen on lithium-copper clusters in a previous study [20].

RESULTS AND DISCUSSION

GEOMETRIES

Fig. 1 shows the optimal geometrical structures of the O_2 -bimetallic cluster systems with the corresponding geometrical parameters. The above mentioned structures were compared with those reported for the bare bimetallic clusters in a previous study [32]. It was observed that when the interaction between the O_2 molecule was realized for Cu-Cu or Cu-K bonds of the bimetallic cluster, the geometry of the cluster was modified weakly. However, when the interaction O_2 was realized for a K-K bond, it produced a strong distortion in the geometry of the bimetallic clusters, thereby conducting to the rearrangement of the atoms of the bimetallic clusters, as observed for $K_2Cu_2O_2$, $K_2Cu_4O_2$ and $K_3Cu_4O_2$ systems in the present study. In addition, the great distortion in the geometry of the bimetallic cluster produced the dissociation of the O_2 molecule in $K_2Cu_4O_2$ and $K_3Cu_4O_2$ systems. The above mentioned latter systems would be discussed in more detail in the next section. Generally, distortions were observed in the local environment, that is, in the region of adsorption of the molecular oxygen. For the most stable systems, the average Cu-Cu and K-Cu distances in $K_mCu_nO_2$ and in bare bimetallic clusters are plotted in Fig. 2. It was

clearly observed that the adsorption of molecular oxygen did not produce any significant changes in the Cu–Cu distance with the exception of the $\text{K}_2\text{Cu}_2\text{O}_2$ system, where rearrangement took place, thereby producing a shortening of the Cu–Cu distance and formation of the Cu–Cu bond. Thus, for average Cu–Cu distances, a shortening of 0.02 to 0.12 Å for $\text{K}_m\text{Cu}_n\text{O}_2$ systems with $m = 1, 2, 4$ and $n = 2$ ($m \neq 2$), 3 ($m \neq 1$), 4 and a stretching of only 0.02 to 0.04 Å for systems with $m = 1, 3$ and $n = 3$ ($m \neq 1$), 4 were produced. The maximum Cu–Cu distance was produced in systems when Cu–Cu was broken, i.e., when $m = n$. In general, with respect to the average distance of K–Cu, a stretching of 0.03 to 0.27 Å was produced, which indicated that the K–Cu distance did not suffer a great distortion under the adsorption of O_2 . For $\text{KCu}_{12}\text{O}_2$ system the behavior is similar, i.e., under the adsorption process the average distance of Cu–Cu is not affected and the average distance K–Cu a stretching of only 0.14 Å was produced. For the bare KCu_{12} is shown in Fig.1k. On the other hand, Fig. 1 showed that the adsorption of O_2 occurred on a bridge site (2-fold coordination) with the O_2 molecule approaching parallel to the adsorption site of each one of bimetallic clusters. This latter occurred in all structures except for bimetallic clusters that suffered rearrangement, $\text{K}_2\text{Cu}_2\text{O}_2(\text{I})$ system, and the dissociation of O_2 molecule, $\text{K}_2\text{Cu}_2\text{O}_2(\text{I})$ and $\text{K}_3\text{Cu}_4\text{O}_2(\text{I})$ systems. Generally, when the structure of bimetallic clusters did not suffer rearrangement, the oxygen molecule was oriented through the K–Cu bond ($\text{KCuO}_2(\text{I})$, $\text{K}_2\text{Cu}_2\text{O}_2(\text{II})$, $\text{KCu}_3\text{O}_2(\text{I})$, $\text{K}_2\text{Cu}_3\text{O}_2(\text{I})$, $\text{K}_3\text{Cu}_4\text{O}_2$, $\text{KCu}_4\text{O}_2(\text{I})$, $\text{K}_4\text{Cu}_5\text{O}_2(\text{II})$, $\text{K}_4\text{Cu}_4\text{O}_2(\text{II})$ and $\text{KCu}_{12}\text{O}_2(\text{I})$). The adsorbed O–O distance varied from 1.30 to 1.34 Å, which was between 7% and 10% longer than the O–O distance in the gas phase (1.22 Å). On the basis of the experimental evidence and other theoretical studies it was proposed that the O_2 was adsorbed on a coordinate site. Thus, it would have a parallel orientation to the Cu(111) surface [34, 35], which was in agreement with the results obtained in the present study. A similar trend was found in a previous study for $\text{Li}_m\text{Cu}_n\text{O}_2$ systems [20]. In all the adsorption systems, the O–Cu distance and the O–K distance varied between 1.91 Å and 2.08 Å and 2.51 Å to 2.63 Å, respectively.

Figure 1. Geometrical structures of $K_mCu_nO_2$ systems. a) KCu_2O_2 , b) KCu_2O_2 , c) KCu_3O_2 , d) KCu_3O_2 , e) KCu_3O_2 , f) KCu_3O_2 , g) KCu_4O_2 , h) KCu_4O_2 , i) KCu_4O_2 , j) KCu_4O_2 , k) $KCu_{12}O_2$ and l) $KCu_{12}O_2$.

Figure 2. Cu-Cu and K-Cu average distances for $K_mCu_nO_2$ clusters and $K_mCu_nO_2$ systems.

ENERGIES AND ELECTRONIC PROPERTIES

The binding energy per atom, adsorption energy, LUMO–HOMO gap, and other properties for $K_mCu_nO_2$ systems are summarized in Table 1. First, the electronic state of each system is consequence of their structures electronic. In bare bimetallic clusters, K_mCu_n , depending if $n + m$ is an even or odd number of atoms, the number of total electrons in the cluster will also be even or odd [32]. It is well known that the ground state for O_2 molecule is a triplet. When the interaction takes place between the bimetallic cluster and the O_2 molecule, the possible ground state for adsorption systems ($K_mCu_nO_2$) can be a doublet, triplet or of higher order. In the present study the lower energy structures of all adsorption systems only presented a doublet or triplet multiplicity. Thus, when $m + n$ is odd the electronic ground state of adsorption system is a doublet and when $m + n$ is even gives a triplet, as we can see in Table 1. Second, the binding energy per atom and the adsorption energy for the most stable systems are shown in Fig. 3. The adsorption energy for the systems, which do not show dissociation of the oxygen molecule have values ranging from 5.7 to 48.6 kcal/mol, with the values being maximum for the $K_2Cu_4O_2$ system. In general, as shown in Fig. 3, the binding and the adsorption energies decrease progressively with the increase in the number of potassium atoms in the bimetallic cluster. However, KCu_2O_2 , $K_2Cu_3O_2$, KCu_4O_2 and $KCu_{12}O_2$ systems demonstrate the maximum binding energies and coincide with the systems that have the highest adsorption energy. It was also observed that the systems with a minimum binding energy coincided with the systems that had the lowest adsorption energy, i.e., for $KCuO_2$, KCu_3O_2 , $K_3Cu_3O_2$, and $K_4Cu_4O_2$ systems. Third, in general, a high reactivity towards the O_2 molecule, was observed for $K_mCu_nO_2$ systems when $m = n - 1$, which presented high adsorption energy. The minor reactivity was observed for systems when $m = n$, which presented low adsorption energy and low binding energy. In addition, when $m = n$, the adsorption of O_2 was preferably produced on the K-Cu bond, while the adsorption energy decreased with an increase in the size of the bimetallic clusters. The Cu-Cu bonds were broken in the above mentioned cluster. The K_2Cu_2 cluster was the exception, where the adsorption of O_2 was preferable on the K-K bond as a product of the rearrangement of the bimetallic cluster, thereby producing the formation of the Cu-Cu bond as well as a significant increase of the adsorption energy. In addition, in the systems with $n > m$ and the Cu-Cu bonds not broken, the adsorption of O_2 was also preferable on the K-Cu bond, with the exception of $K_2Cu_3O_2$, $K_2Cu_4O_2$ and $K_3Cu_4O_2$ systems, where the adsorption of O_2 was preferably produced on the K-K bond. In the above mentioned latter systems, the adsorption energy increased with an increase in the size of the bimetallic cluster. The adsorption energy and charge transfer towards the O_2 molecule are shown in Fig. 4. The charge transfer was calculated from NBO results, from the computation of the difference of net charges between components of the system, the bimetallic cluster and the O_2 molecule, with and without interaction. In general, it was observed that there was a good correlation between the above mentioned properties. Thus, systems that presented high charge transfer also presented high adsorption energy. This behavior was observed for $K_2Cu_3O_2$, KCu_4 and $K_3Cu_4O_2$ systems. The minor charge transfer was observed for systems with $m = n$, where the Cu-Cu bonds were broken, which presented the smallest adsorption energy. The exception was for the $K_2Cu_2O_2$ system, in which the system suffered rearrangement as mentioned above, thereby producing formation of the Cu-Cu bond and a high charge transfer. Fourth, in general, the adsorption of O_2 on the Cu-Cu bond was less effective in comparison to the adsorption on the K-Cu bond, in which a decrease between 23 to 56% of the adsorption energy was observed in KCu_2O_2 , KCu_3O_2 , KCu_4O_2 and $KCu_{12}O_2$ systems. Fig. 5 also demonstrated another good behavior when the values of the O–O distance and the charge transfer towards the O_2 molecule were compared. It was indicated that the greater the charge transfer, the greater was the O–O distance. In addition, from Table I the O–O frequency of the adsorbed O_2 molecule showed values ranging from 1122.3 cm^{-1} to 1234.4 cm^{-1} , which was between 25% and 32% lower than the O–O frequency for O_2 in the gas phase (1647.5 cm^{-1}). The above mentioned behaviors explained that the charge transfer from bimetallic clusters to empty $O_2 \pi_{2p}^*$ orbitals weakened the O–O bond, thereby causing an elongation of up to 10% in comparison to its gas-phase length, as mentioned in the previous section, and also reduced its stretching frequency. On the other hand, values ranging from 0.61e to 0.94e for the charge transfer from bimetallic cluster towards the O_2 molecule were found. Thus, above results are indicative with the formation of a superoxo-like specie (O_2^-) under the adsorption process [35].

Table 1. Binding energies (E_b), adsorption energies (E_{ad}), gap between frontier orbitals, LUMO-HOMO (ΔE_{L-H}), O-O bond ($R(O-O)$), O-O stretching frequency ($\nu(O-O)$), and electronic ground state, being $n, m=1-4$ and $w=m+n+2$ for $K_mCu_nO_2$ adsorption systems.

	E_b/w (eV)	E_{ad} (kcal/mol)	ΔE_{L-H} (eV)	$R(O-O)$ (Å)	$\nu(O-O)$ (cm^{-1})	Ground State
$KCuO_2$	1.90	18.9	1.92	1.33	1180.6	$^3A''$
KCu_2O_2 (I)	1.99	46.4	2.80	1.34	1187.7	$^2A''$
KCu_2O_2 (II)	1.77	20.6	2.54	1.33	1169.8	2A_2
$K_2Cu_2O_2$ (I)	1.79	30.5	1.56	1.34	1234.4	3B_2
$K_2Cu_2O_2$ (II)	1.69	17.7	1.87	1.32	1182.8	$^3A''$
KCu_3O_2 (I)	1.83	21.5	1.59	1.33	1176.9	$^3A''$
KCu_3O_2 (II)	1.75	10.6	1.89	1.34	1142.3	$^3A''$
$K_2Cu_3O_2$ (I)	1.83	48.6	2.42	1.34	1233.7	2A_2
$K_2Cu_3O_2$ (II)	1.77	38.7	2.53	1.34	1177.1	$^2A''$
$K_3Cu_3O_2$	1.57	14.8	1.87	1.32	1182.6	$^3A''$
KCu_4O_2 (I)	1.90	45.2	2.85	1.34	1202.1	$^2A''$
KCu_4O_2 (II)	1.83	34.9	2.66	1.34	1157.4	2A_2
$K_2Cu_4O_2$ (I)	1.82	42.2	0.45	-	-	3B_2
$K_2Cu_4O_2$ (II)	1.75	28.3	1.17	1.34	1173.0	$^3A''$
$K_3Cu_4O_2$ (I)	1.82	67.6	1.11	-	-	$^2A'$
$K_3Cu_4O_2$ (II)	1.69	40.8	2.04	1.34	1189.7	2A
$K_4Cu_4O_2$	1.54	14.2	1.98	1.32	1182.1	$^3A''$
$KCu_{12}O_2$ (I)	1.88	29.3	1.29	1.34	1194.1	2A_1
$KCu_{12}O_2$ (II)	1.83	13.1	1.76	1.35	1122.3	$^2A''$

The LUMO-HOMO gap is shown in Fig. 6 and is compared with the adsorption energy for $K_mCu_nO_2$ systems with respect to the number of potassium and copper atoms in the bimetallic cluster. The above mentioned gap is a measure of the molecular hardness [36] and it is commonly used to explain reactivity trends in molecules. In general, it was observed that systems presenting high adsorption energy, presented a large gap, i.e., the adsorption systems were inclined to increase the molecular hardness, thereby producing a high reactivity towards the O_2 molecule. Fig. 7 also demonstrated the difference in gaps between $K_mCu_nO_2$ and K_mCu_n systems and the adsorption energy. In general, it demonstrated a good behavior for the above mentioned two properties indicating that the greater the difference in the gap, the greater is the adsorption energy. The largest difference in the gap was observed for KCu_2O_2 , $K_2Cu_3O_2$, KCu_4O_2 , $K_3Cu_4O_2$ and $KCu_{12}O_2$ systems with $m + n$ as the odd number of atoms, i.e., for systems with an odd number of electrons, thereby presenting high reactivity towards the molecular oxygen. In the remaining systems, the difference between gaps was presented as negative values, i.e., the gap ($K_mCu_nO_2$) was smaller than the gap (K_mCu_n), thereby showing a low reactivity to the adsorption of molecular oxygen.

In base to the above results, we can see that the behavior for adsorption of O_2 on a bigger bimetallic cluster (KCu_{12}) is similar to smaller bimetallic clusters, with the difference that a bigger bimetallic cluster trend to be more stable under adsorption process, i.e., only smallest distortions in the geometry of the bimetallic cluster was found.

In continuation, the rearrangement process was analyzed in detail. In general, the adsorption on the K-K bond produced rearrangement of the atoms of the bimetallic cluster, thereby decreasing the distance of the K-K bond. Thus, the rearrangement of system I of $K_2Cu_2O_2$ was produced for a decrease of K-K and formation of the Cu-Cu bond, as shown in Fig 8a. For the case system I of $K_2Cu_4O_2$, the K atoms on and under the plane formed for the Cu atoms, moved towards a side of the Cu plane, thereby decreasing the K-K distance. This allowed an interaction more favorable with the O_2 molecule and finally produced the dissociation, as shown in Fig 8b. The rearrangement of the system I of $K_3Cu_4O_2$ was produced for the compression of the bimetallic cluster, in a way that favored the interaction of K atoms with the O_2 molecule, thereby producing a decrease of the distance K-K. The rearrangement produced a strong interaction with the O_2 molecule, conducting finally to the dissociation, as in the previous case. It was concluded that the rearrangement produced a great stability of the adsorption system, thereby presenting a higher adsorption energy and binding energy in comparison with the system without rearrangement.

Figure 3. Binding energy per atom and adsorption energy for $K_mCu_nO_2$ systems with $w=m+n$.

Figure 4. Adsorption energy and charge transfer for $K_mCu_nO_2$ systems. The charge transfer goes from K_mCu_n cluster towards the O_2 molecule.

Figure 5. O-O bond distance and charge transfer for $K_mCu_nO_2$ systems

Figure 6. Gap between frontier orbitals, LUMO-HOMO (ΔE_{H-L}), for $K_mCu_nO_2$ systems.

Figure 7. Charge transfer and difference of gaps ($\Delta E_{G2-G1} = G2(K_mCu_nO_2) - G1(K_mCu_n)$; $Gp = E_{LUMO} - E_{HOMO}$; $p=1,2$).

COMPARISON BETWEEN THE $K_mCu_nO_2$ AND $Li_mCu_nO_2$ SYSTEMS

A theoretical study of the adsorption of molecular oxygen on lithium-copper clusters was recently reported [20]. In the following section, the similarities and the differences between the $K_mCu_nO_2$ and $Li_mCu_nO_2$ systems were analyzed. First, the adsorption energy in the $K_mCu_nO_2$ systems was slightly smaller in comparison with $Li_mCu_nO_2$, in which the average values of 29.5 and 37.1 kcal/mol were found, respectively. However, in $K_mCu_nO_2$ a bigger probability of dissociation was produced, that is two systems in comparison with only one in the $Li_mCu_nO_2$ system, with a significantly smaller amount of formation energy. For example, the maximum dissociation energy for the $K_3Cu_4O_2$ system was 67.6 kcal/mol, which was almost half of the energy found for the $Li_2Cu_3O_2$ system. Also, a bigger number of stable systems were found in $K_mCu_nO_2$ systems in comparison to $Li_mCu_nO_2$ systems, with a minor energy cost, i.e., minor adsorption energy. Thus, K_mCu_n clusters would present a bigger reactivity toward the adsorption of oxygen in comparison with the Li_mCu_n clusters. Second, in both systems, $K_mCu_nO_2$ and $Li_mCu_nO_2$, the interaction of molecular oxygen was parallel to the bimetallic cluster, with the oxygen molecule being adsorbed on a bridge site (2-fold coordination).

Figure 8. Rearrangement mechanism for: a) $K_2Cu_2O_2$ and b) $K_2Cu_4O_2$ systems.

However, in the $K_mCu_nO_2$ systems, the O_2 was preferably adsorbed on K–Cu or the K–K bonds, whereas in $Li_mCu_nO_2$ systems the O_2 was only preferably adsorbed on Li–Cu bonds. Third, in both systems, an effective charge transfer was produced from the cluster to the oxygen molecule, which was decisive for the most effective interaction between the cluster and the O_2 molecule as well as the high reactivity observed for both types of clusters. However, in $K_mCu_nO_2$ systems a larger number of stable isomers were observed, which indicated that the reactivity towards the O_2 molecule of K_mCu_n clusters could be higher than Li_mCu_n clusters. Fourth, a good correlation was observed in both systems between the HOMO–LUMO gap and the difference in the gaps with the adsorption energy. This indicated that a most favorable interaction of O_2 with each bimetallic cluster was produced when the adsorption system evolved towards an increase of the gap (or the difference of gaps), thereby producing high adsorption energy, i.e., a high reactivity towards the oxygen molecule. However, the difference of gaps in $K_mCu_nO_2$ systems is bigger than in $Li_mCu_nO_2$ systems, thereby indicating that the adsorption of O_2 on the K_mCu_n clusters produced adsorption systems that are more stable than $Li_mCu_nO_2$. Fifth, it was observed that in both systems the increased reactivity towards the oxygen molecule was produced for the cluster with $m + n$ equal was an odd number of atoms, while the minor reactivity towards the oxygen molecule was produced for the cluster when $n + m$ was an even number of atoms. An odd number of atoms implied an electronic structure of the open shell. Therefore, the bimetallic clusters presenting this electronic structure favored the reactivity and increased the charge transfer towards the O_2 molecule. The presence of the charge transfer in both systems indicated that the interaction between O_2 and the bimetallic cluster occurred by a chemisorption process. Sixth, in $K_mCu_nO_2$ systems a greater rearrangement was observed in comparison to $Li_mCu_nO_2$ systems, with a tendency to produce the dissociation of the O_2 molecule. This indicated that K_mCu_n clusters were less stable than Li_mCu_n clusters. However, the rearrangement mechanism was used in both bimetallic clusters, Li_mCu_n and K_mCu_n , to produce a more stable adsorption system. Finally, in both systems a decrease of the O–O frequency of the order of 28% with respect to the O–O frequency for O_2 in the gas phase (1647.5 cm^{-1}) and an increase of the O–O distance of about 10% were observed. This was indicative that the adsorption on the bimetallic cluster favored the dissociation to the O_2 molecule. Also, for both systems, $K_mCu_nO_2$ and $Li_mCu_nO_2$, from the analysis of the O–O frequency of the adsorbed O_2 molecule and charge transfer from bimetallic cluster towards

the O_2 molecule, the results are consistent with the formation of a superoxo-like specie (O_2^-) under the adsorption process [35]. Thus, the obtained results could be imported to future applications of the bimetallic clusters in the catalytic processes.

CONCLUDING REMARKS

The adsorption of molecular oxygen on small bimetallic K_mCu_n clusters was theoretically studied, and their properties were analyzed and compared with those found for the adsorption of O_2 on bimetallic Li_mCu_n clusters, as reported in a previous study [20]. It was found that the reactivity of O_2 on K_mCu_n clusters was greater than that of Li_mCu_n clusters, as a base to a bigger number of isomers found for the adsorption system and the minor formation energy to produce the rearrangement of the atoms in the bimetallic cluster. In both systems, $K_mCu_nO_2$ and $Li_mCu_nO_2$, the alkali atoms in bimetallic clusters had the finality to increase the charge of the copper atoms and produce a more effective charge transfer towards the O_2 molecule. The presence of the charge transfer indicated that the adsorption was produced by a chemisorption process. Thus, the interaction of O_2 with the bimetallic cluster was of a local nature. In general, the optimum interaction of the O_2 molecule with X_mCu_n ($X = Li, K$) in both systems was produced when the number of alkali atoms was $m = n - 1$. When $m = n - 1$ the Cu–Cu bonds are not broken and the adsorption system present the higher charge transfer, having as consequence the higher reactivity of bimetallic clusters towards the O_2 molecule. On the other hand, when $m = n$ the Cu–Cu bond were broken and the adsorption system presented the minor charge transfer, producing a minor reactivity towards O_2 molecule. The molecular oxygen was adsorbed on bridge sites (2-fold coordination), parallel to the adsorption site, preferably along K–Cu or K–K bonds in K_mCu_n clusters and along Li–Cu bonds in Li_mCu_n clusters.

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