

## Quantum-chemical Calculations of the Adsorption of CO on the Metal Oxide Clusters

E.A. Koblova<sup>1,\*</sup>, A.Yu. Ustinov<sup>1,2</sup>, O.L. Shcheka<sup>2</sup>

<sup>1</sup> *Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, 159, 100-letiya Vladivostoka prosp., 690022 Vladivostok, Russian Federation*

<sup>2</sup> *Far Eastern Federal University, 8, Sukhanova st., 690950 Vladivostok, Russian Federation*

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The geometric, energetic, spectral and electronic properties of the most stable clusters of the aluminum, nickel and copper oxides with the adsorbed CO molecule have been studied using Density Functional Theory. The obtained results showed the better adsorption properties of nickel oxide clusters. According to the obtained results, the adsorption activity of the examined clusters decreases in the following order: NiO > Al<sub>2</sub>O<sub>3</sub> > CuO. The stronger interaction between active centers of the nickel oxide clusters and CO molecule is attributed to the higher charge transfer from the adsorbate to the surface in comparison with other clusters. The optimal position for CO interaction with the metal oxide surfaces and the appropriate optimal M-CO and C-O bond distances are presented.

**Keywords:** Cluster, Metal oxide, CO, Adsorption, Quantum-chemical calculations.

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### 1. INTRODUCTION

The industrial revolution leads to the one of the most urgent problems nowadays – environmental pollution. A major atmospheric pollutant is carbon monoxide. The total amount of CO emissions in Russia reaches 15 thousand tons per year, two thirds of which is accounted with motor transport. This fact causes the growing interest to the development of catalytically active systems, namely, active in the oxidation of CO to CO<sub>2</sub>.

Catalysts on metal supports are widely used in various reactions as they are characterized by high thermal conductivity and mechanical strength. The promising catalysts for CO oxidation are transition metal based catalysts, which demonstrate high activity, stability, selectivity and are more accessible in comparison with the well-known noble metal based catalysts.

Recently it was found that oxide layers containing 3d-metals such as Ni and/or Cu prepared on valve metals (Al, Ti, etc.) using the method of plasma electrolytic oxidation (PEO) [1] exhibit high catalytic activity in the oxidation of CO to CO<sub>2</sub> [2, 3]. Investigations carried out by X-ray photoelectron spectroscopy showed that PEO-coatings are complex in composition and structure [4, 5] and its catalytic activity strongly depends on the composition and structure of the surface layers. Based on the data obtained, some assumptions about the factors responsible for the catalytic activity of the coatings have been made. The systematic study of the properties and occurring process can be very useful in the future. As we assume, 3d-metal based PEO-coatings can be used in internal combustion engines and industrial processes for the afterburning of discharge gases.

To clarify the details and various aspects of catalytic activity a powerful tool in the form of quantum-chemical modeling can be used. With its help it is possible to obtain accurate information on the energetics and kinetics of the process, nature and structure of active centers, adsorption and desorption properties, etc.

In this paper we present the results of quantum-chemical calculations of the metal oxides which are the main structural components of the real PEO-coatings, and their interaction with CO.

### 2. MATERIALS AND METHODS

There are essentially two approaches in modeling materials and structures. The first one, periodic approach, deals with the periodic systems: atomic layers, bulk crystals, etc by means of setting up a primitive unit cell and periodic boundary conditions. This approach is good for modeling the material's electronic structure but it is rather difficult to study the unsaturated atoms, whereas bulk properties are described by the core atoms of the cluster [6]. The second one, cluster approach, allows to cut out from the surface some atomic or molecular fragment – “cluster” and consider it as a “big molecule” [7]. This approach allows to obtain quite accurate calculations which are much less time- and resource-consuming in comparison with the periodic approach. Its effectiveness has been shown for a large number of systems and process, including physical phenomena associated with short-range order [8] and chemical phenomena of local character [9], as for example, the adsorption of CO on metal oxide surfaces.

Theoretical clusters should not be confused with the experimental ones. Experimental clusters are specific atomic aggregates that exist experimentally while theoretical ones represent the molecular systems, which may or may not exist experimentally and are used to describe characteristics and properties of “big molecules” [9].

All the calculations were carried out within the GAMESS-US package [10] using the hybrid functional B3LYP [11, 12] and the split-valence basis sets: 6-31G\*, 6-31+G\*, 6-311+G\* in cluster approach. Comparison of the results obtained using various methods showed that the exchange-correlation func-

\* [les@ich.dvo.ru](mailto:les@ich.dvo.ru)

tional B3LYP with the split-valence basis sets are applicable for the modeling of real surfaces.

To study the adsorption of CO on metal oxide surfaces, the most stable neutral clusters of aluminum, nickel and copper oxides have been used. We examined  $(\text{Al}_2\text{O}_3)_n$  and  $(\text{NiO})_n$  clusters in a singlet spin state, and  $(\text{CuO})_n$  clusters with various multiplicity: singlet and triplet states for  $n$  even, and doublet and quartet states – for  $n$  odd. For the nickel oxide clusters, there is a convergence problem during optimization of the geometry in a triplet state that we still have not solved.

In order to determine the optimum conditions for CO interaction with clusters, various potential active centers and various positions of CO have been observed. The joint system [cluster+CO] was fully optimized without symmetry constraint. To evaluate the metal oxide surfaces to adsorb CO molecules, the adsorption energy was calculated using the following equation:

$$E_{ads} = [E(\text{cluster} + \text{CO}) - E(\text{cluster}) - E(\text{CO})] - E_{ZPE},$$

where  $E(\text{cluster} + \text{CO})$  is the total energy of the metal oxide cluster with the adsorbed CO molecule,  $E(\text{cluster})$  – the total energy of the bare cluster,  $E(\text{CO})$  – the total energy of carbon monoxide,  $E_{ZPE}$  – zero-point energy. Positive values of  $E_{ads}$  signifies a favorable adsorption and the stability of the joint [cluster + CO] system.

Harmonic vibrational frequency analysis was used to confirm the true minima of the potential energy surface. If no imaginary frequencies were found, the structure was considered to be a global minimum.

### 3. RESULTS AND DISCUSSION

The structure of the metal oxides can be modeled with small clusters. The best agreement of geometric and electronic features of the aluminum, nickel and copper oxide clusters with the available experimental data and the results of other calculations is observed when the cluster size is about 2-8 molecular units [13]. These clusters were used to study the interaction between CO and their active centers.

According to the obtained data, the optimal position for this interaction is the position of CO close to the normal (“zenithal” position), when CO is pointed by carbon to the surface and metal atom is an active center. Depending on the cluster size the calculated adsorption energies that characterize the adsorption of CO on aluminum oxide surface are in the range of 0.79 – 1.73 eV, on nickel oxide – 1.66 – 2.08 eV and 0.15 – 1.35 eV - on the copper oxide surfaces. In further analysis, we will consider the results obtained only for the optimal “zenithal” position of CO towards metal oxide cluster.

#### 3.1 $\text{Al}_2\text{O}_3$ Clusters

The detailed analysis of the geometric features of the joint [cluster + CO] structures showed that the adsorption of CO molecule leads to the decreasing of C-O bond distances when compared to the free CO molecule. This is a result of the electron transfer from the nearby oxygen atoms and CO molecule to the aluminum atom being an active center. The optimized bond

distances are the following:  $R(\text{Al-O}) = 1.743 - 1.870 \text{ \AA}$ ,  $R(\text{Al-CO}) = 2.144 - 2.190 \text{ \AA}$ , and  $R(\text{C-O}) = 1.117 - 1.128 \text{ \AA}$  (Table 1). Reducing of the C-O bond distance on  $0,01 - 0,021 \text{ \AA}$  is a result of charge transfer on  $0.13 - 0.16 e$  from adsorbate to adsorbent for all clusters with  $n = 2 - 8$  except cluster  $n = 5$ , for which this value is  $0.23 e$ . The electron density for the optimized  $\text{CO}/(\text{Al}_2\text{O}_3)_n$  structures is localized between carbon and aluminum atom forming a bonding  $\pi$ -orbital.

**Table 1** – Calculated characteristics of the  $\text{CO}/(\text{Al}_2\text{O}_3)_n$ : adsorption energy  $E_{ads}$  (in eV), bond distances  $R$  (in  $\text{\AA}$ ) and adsorption-induced CO frequency shift  $\Delta\nu$  (in  $\text{cm}^{-1}$ )

$n$	$E_{ads}$	$R(\text{Al-CO})$	$R(\text{C-O})$	$\Delta\nu(\text{CO})$
2	1.39	2.144	1.117	92
3	1.70	2.160	1.117	95
4	1.73	2.162	1.117	95
5	0.79	2.190	1.128	92
6	1.70	2.173	1.117	105
7	1.64	2.180	1.118	86
8	1.63	2.108	1.121	105

The analysis of the frequencies in the IR-spectrum of the clusters with the adsorbed CO molecule can be an effective tool to study the features of the adsorption of CO and evaluate the activity of the potential active centers. The experimentally determined value of the stretching vibrations of CO molecule in the infrared spectra of  $\text{CO}/(\text{Al}_2\text{O}_3)_n$  is near  $2200 \text{ cm}^{-1}$  and strongly depends on the methods of formation and analytical methods examining CO adsorption. This frequency is characteristic and reflect the binding between adsorbate and adsorbent. Our calculated values are in the range of  $2295-2314 \text{ cm}^{-1}$ .

A more efficient characteristic to evaluate the adsorption of CO on some surfaces could be the calculated vibrational frequency shifts of C-O bond in the infrared spectrum. Thus, the structural changes of the aluminum oxide clusters are accompanied with a blue shift of the CO vibrational frequency. These blue shifts compared to the vibrations of the free CO molecule are in the range of  $86-105 \text{ cm}^{-1}$  and points to the stability of the joint [cluster + CO] system. In case when CO molecule is pointed with oxygen atom to the surface, the adsorption bands in the IR-spectra are red shifted on  $45-86 \text{ cm}^{-1}$ .

#### 3.2 NiO Clusters

The adsorption of CO on nickel oxide clusters is characterized by shorter metal-CO ( $1.748-1.862 \text{ \AA}$ ) and, on the contrary, longer C-O bond distances ( $1.140-1.157 \text{ \AA}$ ) in comparison with the adsorption of CO on the aluminum oxide clusters. The charge transfer that in general leads to the better binding between active center of the cluster and CO molecule is higher for the nickel oxide clusters ( $0,02-0,16 e$ ) than for the aluminum ones. As a result, greater values of the adsorption energies are observed (Table 2). These data are in a good agreement with the experimental results that showed the higher catalytic activity of the Ni-containing PEO-coatings, the main structural components responsible for their catalytic activity of which seems to be nickel oxide structures.

**Table 2** – Calculated characteristics of the CO/(NiO)<sub>n</sub>: adsorption energy  $E_{ads}$  (in eV), bond distances  $R$  (in Å) and adsorption-induced CO frequency shift  $\Delta\nu$  (in cm<sup>-1</sup>)

$n$	$E_{ads}$	$R(\text{Ni-CO})$	$R(\text{C-O})$	$\Delta\nu(\text{CO})$
2	1.97	1.754	1.145	-45
3	1.66	1.748	1.143	-32
4	1.96	1.768	1.147	-59
5	1.68	1.760	1.145	-58
6	2.08	1.779	1.140	-17
7	1.72	1.754	1.144	-37
8	1.72	1.862	1.157	-151

The adsorption of CO molecule on the nickel oxide surface leads to the intense band in the infrared spectrum near 2143 cm<sup>-1</sup> [14]. The values of the stretching vibrations of CO molecule in the calculated IR spectra are in the range 2058-2191 cm<sup>-1</sup>. The absorption bands in the calculated IR spectra of CO/(NiO)<sub>n</sub> clusters are shifted to the region with lower frequencies compared to the vibrations of the free CO molecule on 17-151 cm<sup>-1</sup>.

Both stretching vibrations of CO molecule in the infrared spectra of CO/(NiO)<sub>n</sub> and the adsorption-induced CO frequency shifts are in a good agreement with the known literary data. The value of the  $\Delta\nu$  calculated earlier for the adsorption of CO on the NiO(100) surface with the use of the functional B3LYP was -73 cm<sup>-1</sup> [15].

### 3.3 CuO Clusters

The worse adsorption of CO is occurred on the copper oxide clusters. The calculated adsorption energies for clusters with  $n = 3-8$  are in the range of 0.15-0.21 eV. The maximum  $E_{ads}$  value of 1.35 eV is observed for the minimal (CuO)<sub>2</sub> cluster. In this case the bond distance between active center and CO is 1.819 Å. In other cases, for  $n = 3-8$  the distance between active center and CO is in the range of 2.292-2.439 Å indicating the absence of the binding between CO and a cluster. At that, C-O bond distances does not change much.

The calculated adsorption energies, bond distances and the adsorption-induced CO frequency shifts for the most stable copper oxide clusters are listed in Table 3. The adsorption of CO on copper oxide clusters is characterized by both blue and red shifts in the IR-

spectrum. The high-spin state of (CuO)<sub>n</sub> clusters with  $n = 4-8$  is characterized by the positive values of the adsorption-induced CO frequency shifts  $\Delta\nu(\text{CO})$  that indicates to the higher activity of the corresponding adsorption centers.

**Table 3** – Calculated characteristics of the CO/(CuO)<sub>n</sub>: adsorption energy  $E_{ads}$  (in eV), bond distances  $R$  (in Å) and adsorption-induced CO frequency shift  $\Delta\nu$  (in cm<sup>-1</sup>)

$n$	$E_{ads}$	$R(\text{Cu-CO})$	$R(\text{C-O})$	$\Delta\nu(\text{CO})$
2	1.35	1.819	1.142	-35
3	0.21	2.301	1.141	-34
4	0.15	2.399	1.141	23
5	0.33	2.319	1.140	28
6	0.17	2.439	1.141	13
7	0.51	2.292	1.142	16
8	0.20	2.357	1.141	28

The lower catalytic activity of the copper oxide clusters can be also attributed to the lower charge transfer from CO molecule to the surface (0.01 – 0.15  $e$ ) in comparison with the nickel or aluminum oxide clusters.

## 4. CONCLUSIONS

Within the present study, we examined the geometric, energetic and spectral features of the (Al<sub>2</sub>O<sub>3</sub>)<sub>n</sub>, (NiO)<sub>k</sub> and (CuO)<sub>p</sub> clusters during their interaction with CO. According to the calculated values of the adsorption energy, the adsorption activity of the examined clusters decreases in the following order: NiO > Al<sub>2</sub>O<sub>3</sub> > CuO. The average value of the adsorption energy for the nickel oxide clusters (NiO)<sub>n</sub> ( $n = 2-8$ ) is 1.83 eV, aluminum oxide (Al<sub>2</sub>O<sub>3</sub>)<sub>n</sub> – 1.51 eV oxide copper (CuO)<sub>p</sub> – 0.42 eV. The obtained results showed the better adsorption properties of nickel oxide clusters. The stronger interaction between active centers of the nickel oxide clusters and CO molecule is attributed to the higher charge transfer from the adsorbate to the surface.

The obtained results shed light on the features of the adsorption of CO on metal oxide surfaces, confirm and explain the better catalytic activity of the nickel oxide structures and will be generally useful for future design of materials active in CO to CO<sub>2</sub> oxidation.

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