

## A Theoretical Study of CO Adsorption on Pt-Me (Me- Fe, Co, Ni) Nanoclusters

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### Abstract

We used DFT calculations to study interaction of carbon monoxide with platinum binary nanoclusters of core-shell structure  $Pt_{42}X_{13}$  (where X - transition metals Fe, Co, Ni). Bond strength was calculated for CO adsorption on a platinum monolayer as well as and regularities of the core (Fe, Co, Ni) of binary nanocluster influence on geometry and energy behaviors of the adsorption. On the ground of data obtained we proposed a mechanism of CO interaction with platinum binary nanoclusters. The mechanism is based either on electronic properties changes for surface platinum atoms under the influence of our core or on distribution changes for active adsorption centers in dependence on the core nature.

**Keywords:** Platinum binary nanoclusters; Adsorption; Carbon monoxide; Density functional theory method; Bond energy

### Introduction

In catalytic electrodes, manufactured for low temperature fuel cells, to decrease their prices, binary nanoclusters PtX (X - Cr, Fe, Co, Ni and others) are often used. According to literature [1-3], such binary nanoclusters may possess higher catalytic activity, than pure metals. However, if hydrogen (obtained by hydrocarbon conversion) is used as a fuel, effective work of catalysts is dramatically decreased due to poisoning of nanoclusters by carbon monoxide admixtures. Thus, although high initial catalytic properties of such binary nanoclusters, their stability and corrosive resistance dramatically drops. Even tiny amounts of CO poison platinum anode after blocking active centers and reaction depletion. Many publications of the last years were devoted to the problem of adsorption and oxidation of CO on anodic catalysts for fuel cells [4-6]. These works were directed on search of experiments and theoretical data to propose and understand the mechanisms of CO adsorption and its poisoning of different nanocatalysts. Calculations help to 'realize' reaction conditions in a more simple way as compared with experiments [7]. Some problems may be solved through understanding of micro-mechanisms of atom and molecular interaction with nanocatalysts, when theoretical mechanisms for adsorption are understood. Besides proposition of structural and electron reasons of poisoning may be accepted [8-10]. But theoretical approaches in modern modeling often give doubt information, whereas the methods themselves cannot describe nanocluster properties in a correct way due to neglecting of quantum nature of interaction in such systems. Quantum-chemical methods describe surface structure, sizes and composition of nanoclusters in thin details, which sufficiently changes both catalytic activity and corrosive resistance of nanocatalysts. The aim of such investigation for practice is atomic and molecular mechanism of CO interaction with functional platinum catalysts, which help optimized choice of surface morphology of the surface and nature of binary nanocluster catalyst for fuel cells, which are stable to CO. In this occasion an estimation of micro- mechanisms of CO location on surfaces and effects of electronic structure of CO on metal nanoparticles. First principles studies of additional elements influence on CO adsorption on Pt alloys confirmed [11] the role of stresses, induced by such elements, when electronic states on platinum are changed, followed by CO adsorption energy decrease. Further studies [12] confirmed Pt stability to CO poisoning as a result of adsorption energy decrease through CO depletion from platinum active centers. In the present work the process of CO adsorption on

platinum binary nanoclusters  $Pt_nX_m$  (X - transition metals Fe, Co, Ni) was studied and their resistance to CO poisoning in the environment of low temperature fuel cells was estimated on the basis of quantum-chemical energy parameters comparison.

### Computational Details

Platinum binary nanocluster were simulated on the basis of Pt real crystal lattice (f.c.c. with lattice parameter 3.92 Å), when atoms were closed packed. From many possible structures one of the most packed is a cubo-octahedron  $Pt_{55}$ , (Figure 1a), constructed from eight elementary f.c.c. lattices of platinum with full symmetry and maximum surface. The choice is motivated by the following reasons:  $Pt_{55}$  nanocluster has four coordinate spheres of its surface; the nanocluster is the most stable one due to both quantum-chemical studies [13,14] and mass spectroscopy measurements [15]. Neighbor number in a cubo-octahedron is the greatest in comparison with other structures and causes its stability.

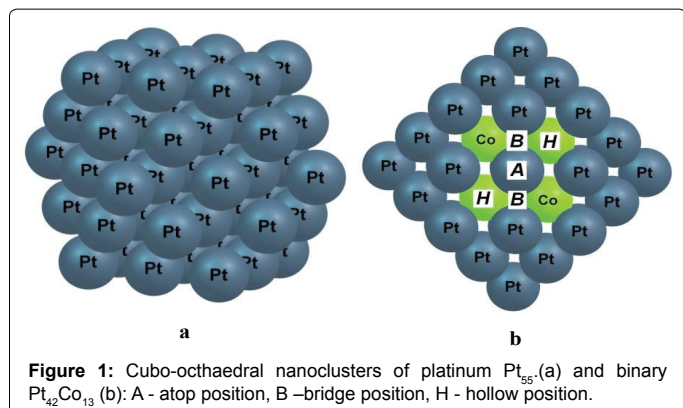
Our structures were formed as «core-shell» particles, where inner core had atoms of a transition metal (secondary component of the nanocluster), while the shell in one atomic layer was built of platinum as an active catalyst (Figure 1b). Our own [16] and other author [17] studies showed, that the core influence sufficiently on the nanocluster catalytic and corrosive behaviors. Particularly, nanoclusters PtCo with the core-shell structure possesses enhanced catalytic activity and stability to oxide formation during their electro-reduction on cathodes of low temperature fuel cells. Enhanced activity in PtCo obeys to reaction ability of the nanocluster surface to oxygen reduction as well as to the strength of chemo-sorption bonds of the surface with atomic oxygen. Besides, a reactive center position in three-fold sites at the surface should be centered by Co atom in the sub layer. On the other hand similar nanoclusters may possess higher stability in aggressive sour environment, which causes electro-chemical corrosion of a catalyst material.

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In the present work we studied processes of platinum stable nanoclusters and binary nanoclusters  $Pt_nX_m$  (X - Fe, Co, Ni; n=42; m=13) interaction with carbon monoxide. The nanoclusters were of the core-shell structure.

Electronic structure of geometry optimized binary nanocluster was calculated in the frame of the NWChem 6.1.1 [18] program with the use DFT method in GGA approximation [19] for exchange-correlation functional PW91 and double- $\zeta$  basis set with DZVP polarization [20]. Oxygen and carbon had the 6-31 G\*\* basis sets. The bond energy of CO molecule with a nanocluster surface was found as a change of total energy of our nanocluster system during the molecule approach to the surface. Thus, potential curves were obtained with minima of initial and final stable states and maxima of transition states. Bond energy  $H$  was a difference between total energy of the system nanocluster-adsorbate and sum of total energies of nanocluster and adsorbate  $H = W_{Pt(PtX)CO} - (W_{Pt(PtX)} + W_{CO})$ .

## Results and Discussion

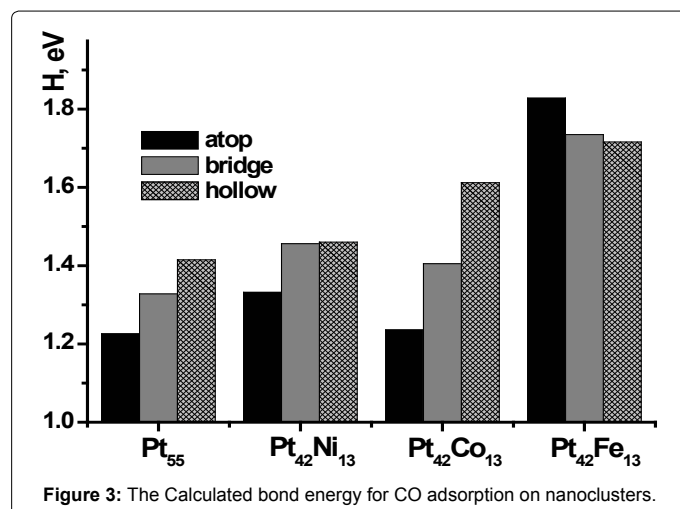
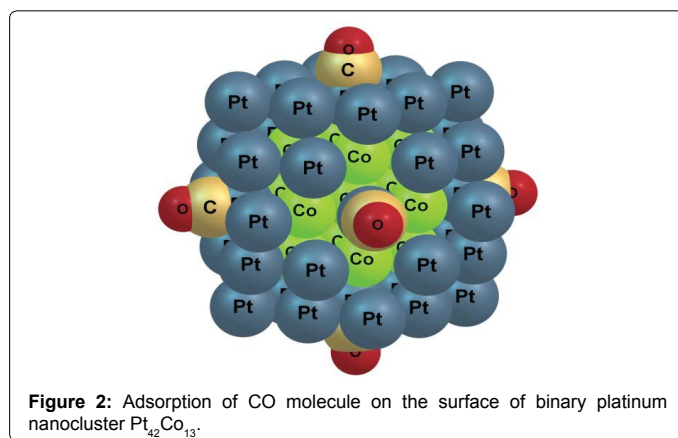
Firstly we have calculated geometry and electronic properties of a single carbon monoxide molecule. Molecular orbital theory predicts electronic structure of the molecule for ten valence electrons as  $[(\sigma_s)^2(\sigma_s^*)^2(\pi_x)^2(\pi_x^*)^2(\sigma_z)^2]$  [21]. CO parameters are as follows: bond order 3, bond length 1.13 Å, ionization potential 14.1 eV, bond energy 256 kcal/mole, vibration frequency 2150 cm<sup>-1</sup>. Carbon monoxide forms coordination bonds with transition atoms metals by its carbon atom, whereas these metals are able to  $\sigma$ - and  $\pi$ -interaction [22]. We calculated bond distance between C and O in the molecule by different methods (Table 1). Variation in this approximation with different basis sets leads to a little deviation from experiments for bond distance in CO, even for less exact semi-empirical method PM6.

During calculations of CO interaction with pure and binary platinum nanocluster  $Pt_{55}$  only one or two molecules of CO were considered (Figure 2) for surface plane (100) with 9 atoms. Calculations were performed in a perpendicular direction of the newly formed bond, as well as different sites - atop (A), bridge (B) and hollow (H). Adsorption energy, distance of CO from the surface, charges on atoms and distance in the molecule were calculated. All six surfaces (100) of our binary nanoclusters were covered with CO molecules in symmetric sites (see Figure 1b): atop - 6 molecules, bridge and hollow- 12 molecules. After that our nanocluster obtained a high symmetry structure, available for optimization. Binding energies were calculated as being related to values per neighbor atoms, similar to the methodology of the paper [23,24]. Bond energy was calculated as follows. For atop sites it was determined by  $H = [W_{Pt-CO} - (W_{Pt} + W_{CO})]/6$ , while for bridge and hollows

sites  $H = [W_{Pt-CO} - (W_{Pt} + W_{CO})]/12$ . Thus, bond energies were obtained as related to a single molecule of carbon monoxide. As we see (Figure 3), the most favorable site for CO on  $Pt_{55}$  nanocluster is the hollow one, whereas adsorption heat is the biggest for it. It should be noted, that calculated heat of adsorption is in frames of experimental values of adsorption heats for CO on Pt(111) [25].

It should be noted that contradiction experiments exists regarding Pt - CO bond energies and their consideration under low coverage. Some authors accept atop positions as prevailing [26], other authors accept hollows ones [27]. Such discrepancy is explained by different experimental methods, used in determination of adsorption parameters for different conditions (temperature, pressure, surface coverage). Adsorption energy drops to the values of 1.3-1.6 eV. Calculation results showed prevailing adsorption sites as hollow ones [28]. Calculated bond energies, present here, lie in the frames of experimental values of CO adsorption on Pt (111), and coincide with results of others.

The most stable adsorption of CO was observed in the hollow site, as is evidently from the shortest distance from the surface 1.418 Å (Table 2), as well as decrease for CO atomic distance in 10%. Thus, in this site strong bond of CO to the surface occurs without dissociation of the molecule. Really platinum carbonyl compounds have larger bond distances Pt - CO (in decimals) because of more accurate approximation [29,30], used in these studies. Moreover carbonyls with a few CO ligands should enhance bond distances (as compared with low chemisorption), due to steric interactions of these ligands. During adsorption of CO charge on carbon atom growth up in comparison



	Method of calculation					Experiment [23]
	PM6	MP2/6-31G*	MP4/6-311+G(2d, 2p)	B3LYP/LANL2DZ	B3LYP/6-311+G(2d, 2p)	
$d_{CO}$ , Å	1.1396	1.1511	1.1458	1.1665	1.1256	1.13

Table 1: Calculated distance (d) in molecule CO in different methods.

		atop	bridge	hollow
Pt <sub>55</sub>	D, A	1.563	1.542	1.418
	d, A	1.132	1.125	1.112
	q, e	0.446	0.481	0.526
Pt <sub>42</sub> Ni <sub>13</sub>	D, A	1.606	1.533	1.362
	d, A	1.135	1.148	1.169
	q, e	0.542	0.466	0.803
Pt <sub>42</sub> Co <sub>13</sub>	D, A	1.645	1.505	1.323
	d, A	1.286	1.264	1.328
	q, e	0.224	0.450	0.436
Pt <sub>42</sub> Fe <sub>13</sub>	D, A	1.334	1.420	1.635
	d, A	1.115	1.126	1.120
	q, e	0.561	0.628	0.634

Table 2: Calculated geometry of CO adsorption on the surface (111) of nanoclusters, D – distance (C–Pt) of the molecule to the surface, q – charge on atom C, d – atomic distance in CO.

with that of free molecule CO. So, there are no contradiction to the statement [22] that in the case of CO adsorption on homogenous metallic surfaces bond strength depends sufficiently on delocalization of electron charge from filled  $d\pi$ -orbitals of the metal to empty  $\pi^*$ -orbital of CO. This leads to reverse transition of the charge due to donor-acceptor bond with strengthening of the  $\pi$ -bond.

Therefore CO bonding on the surface of platinum nanocluster occurs through donor-acceptor interaction through carbon atom with formation of  $\pi$ - and  $\sigma$ -bonding. To estimate influence of the second component in platinum nanoclusters on its activity in the CO environment, we calculated CO interaction with the surface (111) of binary nanoclusters with core-shell structures. Three kinds of nanocluster Pt<sub>42</sub>Co<sub>13</sub>, Pt<sub>42</sub>Fe<sub>13</sub>, Pt<sub>42</sub>Ni<sub>13</sub> were considered.

Our results confirm influence of binary nanocluster core on surface interaction of Pt atoms with CO molecule. Thus adsorption heat growth for it is observed in a row Pt<sub>55</sub> ≤ Pt<sub>42</sub>Ni<sub>13</sub> < Pt<sub>42</sub>Co<sub>13</sub> < Pt<sub>42</sub>Fe<sub>13</sub> (Figure 3). Obviously, nanocluster ability for CO bonding determinate electron density of the 5d-orbital in connection with surface geometry (dimension effects) and electron interaction of Pt layer on the surface with the core (the ligand effect). Further CO  $\pi^*$ -orbital participation in bond formation depends on energy level gaps of the metal and this orbital. Nearest levels form stronger bonds. Calculated ionization potential for CO  $\pi^*$ -orbital is 5.5 eV, while for metals experimental work functions are as follows: Fe - 7.63 eV, Co - 7.8 eV, Ni - 7.9 Pt - 9.0 eV [31]. The higher the value of work function, the lower bond strength in Pt - CO as a result of increasing energy gap between  $\pi^*$ -level in CO and metal orbital levels.

The strongest bond of CO was observed with the surface of Pt<sub>42</sub>Fe<sub>13</sub> at atop positions, oppose to hollow site position of other nanoclusters. The shortest bond length indicates about strong bond. Bond length increases in a row Pt<sub>42</sub>Fe<sub>13</sub> < Pt<sub>42</sub>Ni<sub>13</sub> < Pt<sub>42</sub>Co<sub>13</sub>, so semi-dissociative state exists for platinum-nickel Pt<sub>42</sub>Ni<sub>13</sub> and full dissociation was found for platinum-cobalt Pt<sub>42</sub>Co<sub>13</sub>. Platinum resistance to CO poisoning depends on adsorption heats, which show the degree of adsorption centers blocking. The presence of nickel has no sufficient effect on platinum shell, while iron or cobalt in the core decreases platinum resistance to CO poisoning. Such a behavior of Pt<sub>42</sub>Ni<sub>13</sub> during its interaction with

CO may be described by ligand mechanism of nickel influence on bonding in Pt-CO through induced charges in electronic structure of platinum surface atoms. In this case  $\pi$ -bonds emerge between surface platinum atoms and neighbors in sublayer due to partly filled d-orbitals of metal. During CO adsorption a concurrence exists regarding d-electrons of surface platinum atom between CO and nickel atom. This is confirmed by essential increase in calculated electron density and Muliken charge on carbon in CO-Pt<sub>42</sub>Ni<sub>13</sub>, than in CO-Pt<sub>55</sub>.

In prevailing situations heat grows up for CO adsorption on binary nanoclusters, compared with pure platinum nanoclusters. Thus, the core induces poisoning of the surface. For Pt<sub>42</sub>Fe<sub>13</sub> a prevailing adsorption of CO is observed in atop sites. This indicates that the core of Fe atom changes electronic behaviors of the catalytic active metal platinum through collective (morphologic) mechanism, when additional component in binary nanoclusters charges distribution of active centers on the surface and allows catalytic reactions to occur. Such a reaction is electrooxidation of hydrogen in bridge and hollow sites.

During interaction of surface platinum with nanocluster core a decrease is in overlapping of sublayer d-orbitals (Fe, Co, Ni) and surface (Pt) layers in a sequence Ni>Co>Fe. As a result most surface d-orbitals become free in platinum atoms, which are able to form bonds both with CO and H atoms. Thus, in the initial step during binary nanocluster interaction with CO and H<sub>2</sub> under low coverage of the surface in all adsorption sites a ligand sphere occurs in metal-environment interface. As a result, a strong chemisorptions of H<sub>2</sub> occurs on neighbor free atop positions due to the conjugation effect.

## Conclusions

1. A model of core-shell binary nanocluster Pt<sub>42</sub>X<sub>13</sub> (X - Fe, Co, Ni) poisoning by carbon monoxide was proposed in environment of low temperature fuel cells. The model is grounded on adsorption behavior calculations for CO interaction with nanocluster surfaces and an ability of the nanoclusters to strong bond formation with carbon monoxide in dependence on core nature and adsorption sites.
2. Analysis of calculated adsorption heats, adsorption distances, distances in molecules, electronic charges and densities in the system Me-CO lead to establishment of main physico-chemical behaviors of Fe, Co and Ni influence (core of binary nanoclusters) on their interaction with CO. Especially transition metals Fe, Co and Ni sufficiently influence on formed bond behaviors on the platinum surface layer mainly by two mechanisms: ligand (electronic) mechanism, when Fe, Co and Ni change electronic properties of Pt as catalytically active metal, and collective (morphological) mechanism, where additional component of binary nanocluster changes distribution of active sites on Pt surface with new catalytic reaction ways.
3. It was shown, that Pt<sub>55</sub> has an ability to lower catalytic properties through poisoning by carbon monoxide through formation of strong chemo-sorption bond with the highest adsorption heat, which increases for binary nanoclusters in the sequence Pt<sub>55</sub> ≤ Pt<sub>42</sub>Ni<sub>13</sub> < Pt<sub>42</sub>Co<sub>13</sub> < Pt<sub>42</sub>Fe<sub>13</sub> due to electronic interactions between 5 d-orbital of transition metals and  $\pi^*$ -orbital in CO for increasing ionization potential in the row Fe<Co<Ni.

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