DFT calculation of electric field effect on the energy profile of the CO oxidation reaction catalyzed by Ni nanoparticles

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Abstract. The DFT calculations of energy profiles for the carbon monoxide oxidation reaction in the presence of Ni catalyst in the various electric fields were performed by means of the Gaussian package. In order to do that the simple computational model was suggested for the active sites on the surface of the Ni catalyst prepared by the laser electrodispersion (LED) method. The data obtained demonstrate that the energy barriers on the reaction path, which the reaction kinetics is determined by, may be reducted in the electric field by factor from 12% up to 90%. This result supports the hypothesis, that the spontaneous charge redistribution in the catalytic systems produced by the LED method may affect significantly their catalytic activity.

1. Introduction
A few years ago a new method of nanoparticle producing, called laser electrodispersion (LED), has been developed in our laboratory [1]. In the course of time we and our colleagues has investigated the properties of such nanoparticles made from different metals: their size [2], structure [3], stability [4], electrical conductivity of the films of nanoparticles [5] etc, alongside with possible applications. The interesting results were achieved in the field of chemical catalysis. The discovery of the size effect of the second kind has been reported previously [1] along with the hypothesis about its mechanisms. It suggests, that in the nanoparticle film with the certain surface density the spontaneous charging of nanoparticles is possible, and eventuating electric field might significantly increase chemical reaction rate. In this paper we present a theoretical quantum mechanics computation for the carbon monoxide (CO) oxidation reaction with the Ni catalyst, which is intended to verify the hypothesis. It merits mention that according to the experimental data Ni nanoparticles produced by LED method (LED-Ni) are active as a catalyst for the CO oxidation reaction [6].

2. Computational method and model
In order to estimate the field effects on the catalytic activity and chemical reaction rate we have performed computations of reaction energy profile with the different electric field intensity by means of the DFT method with hybrid exchange-correlation functional B3LYP and polarized basis set 6-31G(d). Calculations on this level of theory are relatively fast, though the results have more qualitative character rather than quantitative. Nevertheless, DFT computations with
similar level of accuracy are of use for qualitative analysis of chemical reactions (e.g. [7]). All computations have been done by the Gaussian package [8].

Each energy profile computation consist in the geometry optimization of the reactants, intermediate and ultimate products and transition states between them. For every optimized geometry the electron system energy and the molecule vibration frequencies were calculated. Frequencies were used to calculate vibrational energies of molecules and their thermochemistry properties such as thermal corrections to energy, enthalpy and Gibbs free energy. They was calculated for the standard conditions (1 atmosphere, 298.15 K).

The intermediates on reaction paths were determined by means of potential energy surface scans, while for the search of the transition states Synchronous Transit-guided Quasi-Newton (STQN) method was used. Also Internal Reaction Coordinate (IRC) calculations were performed after transition state optimizations to verify that the discovered saddle points on the potential energy surface actually connect the minimums of correct reactants, products or intermediates.

2.1. Model of the LED-Ni catalyst

Ab initio methods, DFT including, couldn’t be used for computation of large systems, such as a whole nanoparticle. Therefore it’s necessary to choose some simple model of the catalyst with a small amount of atoms. We’ve based the model on the following considerations:

- Ni on the surface of the nanoparticles was shown to be in $Ni^{2+}$ state by the X-ray photoelectron spectroscopy (XPS) experiments [6]. Furthermore, since the spectra of $Ni^{2+}$ in $NiO$ and in $Ni(OH)_2$ are slightly different, it has been concluded by the spectra that the main state of Ni in the nanoparticles is analogous to the state of $Ni$ in its hydroxide.

- According to the experimental data on CO adsorption on the surface of nickel [9], the ”linear” structure predominates, where CO molecule is linked to a single atom of surface. So it’s probable that at least under certain conditions a single atom of Ni have a dominant role in the process of molecule adsorption and, consequently a dominant role in chemical reaction.

In the light of these facts, the simplest model of catalyst that may be considered for the fast qualitative analysis is the nickel hydroxide — $Ni(OH)_2$.

2.2. The reaction path on the $Ni(OH)_2$

In this paper we decided to consider the reaction with the excess of oxygen, in which case we can assume that the first step on the reaction path is an adsorption of oxygen molecule. The scan of potential energy surface for the different distances between $Ni(OH)_2$ and $O_2$ has shown, that the adsorption may occur without any energy barrier.

As a result, the energy profile for the reaction on catalyst contains energies of the following phases:

(i) $Ni(OH)_2$, separate $O_2$ molecule and two separate $CO$ molecules,
(ii) $Ni(OH)_2O_2$ complex and two separate $CO$ molecules,
(iii) Transition state between $Ni(OH)_2O_2 − CO$ and $Ni(OH)_2 − CO_2$ and a separate $CO$ molecule,
(iv) $Ni(OH)_2O$, a separate $CO_2$ molecule and a separate $CO$ molecule,
(v) Transition state between $Ni(OH)_2O−CO$ and $Ni(OH)−CO_2$ and a separate $CO_2$ molecule,
(vi) $Ni(OH)_2$ and two separate $CO_2$ molecules.

In order to estimate the field effects the optimizations and energy computations for this phases have been done with electric field of various intensity applied. The direction of the electric field has been chosen as illustrated in fig. 1, while the range has been determined according to the
value, that may be calculated as the field between the substrate and a nanoparticle with one extra electron. Since the strong electric field is localized near the charged nanoparticles, it has been taken into account only in the computations with $Ni(OH)_2$, while the separate molecules energies were still estimated without field.

![Figure 1. Field directions. The upper arrow points to the positive direction.](image)

3. Computation results and discussion
For the start, the total reaction heat has been estimated as the enthalpy difference between reactants and products. The value obtained is $\Delta H_{298} \approx -312.8$ kJ/mol. In our model it doesn't depend on the reaction path and the localized electric field, so this value is universal. It may be compared with the tabular value of standard enthalpy of CO combustion $\Delta H_{std} \approx -283.4$ kJ/mol. The difference is relatively small, therefore the qualitative results of the following computations may be considered trustworthy.

![Figure 2. Catalytic energy profiles for the different electric field intensity: $-3.09$ V/nm, $-1.54$ V/nm, 0 and 1.54 V/nm from up to down.](image)

![Figure 3. Structures of the energy minimums and transition states on the reaction path. $E = 0$](image)

Fig. 2 presents the energy profiles for catalytic CO oxidation along with pictures of the $Ni(OH)_2$ complex with adsorbed molecules for the each phase on the reaction path in the fig. 3. There are a few main features on these profiles:

- All phases are lower on the energy scale then the reactants, hence the reaction may proceed along this route.
- The first transformation after oxygen adsorption passes through the significant energy barrier. So it may be assumed that the height of this barrier determines the rate of the reaction.
• The differences between the profiles are relatively small, but they are much larger than a computation error.

As a final result of all computations we want to present the plots for the barrier height percentage changes against the electric field intensity (fig. 4). It can be seen that in the field of the proper orientation the barriers on the reaction path may be reduced by 12% for the first barrier up to 92% for the second barrier. So even though only the former should determines the reaction rate and hence the catalytic activity for this reaction, the computation shows that electric field of spontaneously charged nanoparticle may significantly affect a reaction energy profile.

![Figure 4](image)

Figure 4. The barriers percentage changes against the electric field intensity for the two barriers on the CO oxidation reaction path: •: for the first barrier (main) – – – ♦: for the second barrier.

4. Conclusion
Summing up, in this work the attempt of ab initio computation for the size effect of the second kind was presented for the first time. It was demonstrated, that the relatively simple model of Ni catalyst allow to describe qualitatively the field effects on the reaction energy profile for CO oxidation. Finally, the energy barriers reduction in the electric field was estimated and appears to be reasonably significant. Therefore we can conclude, that the charge state of the catalyst on the substrate indeed has an impact on the chemical reaction rate and hence on the catalytic activity. So the charge redistribution in the catalytic systems is an important factor which should be taken into account in the process of catalyst development.

References
[1] Gurevich S A, Kozhevin V M, Yassievich I N, Yavsin D A, Rostovshchikova T N and Smirnov V V 2007 *Thin films and nanostructure* 34 725-54
[2] Lokteva E S, Peristy A A, Kavalerskaya N E, Golubina E V, Yashina L V, Rostovshchikova T N, Gurevich S A, Kozhevin V M, Yavsin D A and Lunin V V 2012 *Pure Appl. Chem.* 84 495-508
[3] Rostovshchikova T N, Smirnov V V, Kozhevin V M, Yavsin D A, Zabelin M A, Yassievich I N and Gurevich S A 2005 *Applied Catalysis A* 296 70-9
[4] Gurevich S A, Yassievich I N, Kozhevin V M, Yavsin D A, Zabelin M A, Tretyakov P A, Rostovshikova T N and Smirnov V V 2004 *Mat. Res. Soc. Symp. Proc.* 806 725-54
[5] Rumyantsev S L, Levinshtein M E, Gurevich S A, Kozhevin V M, Yavsin D A, Shur M S, Pala N and Khanna A 2006 *Physics of the Solid State* 48 2194
[6] Rostovshchikova T N, Shilina M I, Golubina E V, Lokteva E S, Krotova I N, Nikolaev S A, Maslakov K I and Yavsin D A 2015 *Russian Chemical Bulletin* 64 812-8
[7] Startsev A N, Zakharov I V, Voroshina O V, Pashigreva A V and Parmon V N 2004 *Doklady Physical Chemistry* 399 283-6
[8] Frisch M J et al 2016 *Gaussian, Inc.*
[9] Courtois M and Teichner S J 1962 *Journal of catalysis* 1 121-35