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SIZE EFFECTS IN THE *D*-BAND MODEL OF CO OXIDATION BY GOLD NANOPARTICLES

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Мақолада олтин нанозаррачалари CO молекуларининг оксидланиш кимевий реакциясига нисбатан кучли каталитик фаоллигининг вулкан-шакл ўлчамга боғлиқлиги *d*-банд модели, метал кластерларининг желе модели ва Ферми сатҳининг катализдаги роли асосида муҳокама қилинган. Реакция тезлигининг ўлчамга номонотон боғлиқлиги реагентларнинг адсорбция ва реакция маҳсулотларининг десорбциясининг метал кластерлар Ферми сатҳи ва CO, CO_2 молекулаларининг метал заррачаси билан кимёвий боғининг антибоғ молекуляр орбиталининг фарқининг экспоненциал боғлиқлиги билан тушунтирилган. CO молекулаларининг олтин заррачалари билан CO оксидланиш реакциясига нисбатан фаоллаштирилгани зарядлар ўтиши ва ядровий жараенлар ўртасидаги боғлиқликга асосланган кимёвий реакцияларнинг виброн назарияси асосида муҳокама қилинган.

В работе обсуждается вулканоподобная размерная зависимость необычной каталитической активности наночастиц золота по отношению к реакции окисления CO молекул на основе комбинирования модели *d*-зон, модели «желе» металлических кластеров и роли уровня Ферми в каталитической активности. Скорость реакции немонотонно зависит от размера наночастиц из-за экспоненциальных зависимостей адсорбции реагентов и десорбции продуктов от разностей уровня Ферми металлического кластера и состояний разрыхляющих орбиталей молекул CO и CO_2, образующих химические связи с наночастицей. Происхождение активации CO молекул по отношению к реакции CO окисления наночастицами золота обсуждается в рамках вибронной теории химических реакций, основанной на вибронной связи между переносом заряда и ядерными смещениями.

The volcano-type size dependence of the extraordinary catalytic activity of gold nanoparticles in CO oxidation is discussed on the basis of combination of the d-band model, the jellium model of metal clusters and the role of Fermi level in catalytic activity. The reaction rate depends non-monotonically upon the size of nanoparticles, due to exponential dependences of adsorption of reagents and desorption of products on the differences of the Fermi level of the metal cluster and antibonding states of CO and CO_2 molecules forming chemical bonds with the nanoparticle, respectively. The origin of activation of the CO molecules towards the CO oxidation reaction by gold nanocatalysts is discussed in frame of the vibronic theory of chemical reactions based on the vibronic connection between charge transfer and nuclear processes.

I. INTRODUCTION

One of the unique possibilities of nanotechnologies is the control of properties of nanoparticles by their size [1], in opposite to the approaches when materials are replaced by new materials or modified by impurities to achieve desirable properties. It is remarkable that at the nanometer scale materials can exhibit unique properties completely different from their bulk counterparts. One of such materials is chemically inert bulk gold, becoming active catalysts at the nanometer scale with respect to many oxidation and hydrogenation chemical reactions at more mild conditions than traditional catalysts [2-18]. CO oxidation is one of the important oxidation reactions catalyzed by gold NPs, where non-monotonic size effects were observed in the range of 1–5 nm [3-12]. Among

other factors of the reaction activity of gold NPs established in experiments are supports [5, 6, 10, 11], low coordinated gold atoms [8-10], defects presented at the interfaces [14, 15], a non-metallic nature of gold clusters [5], photon-induced hot electrons [19, 20]. In spite of intense research in this field, theoretical foundations of this nanoeffect, including size effects are much behind those experiments. The mechanism of the reaction has not been completely established yet although many important aspects of the reaction have been theoretically investigated [8-10, 14, 15, 21, 22]. In this study, we will show that a volcano-type size dependence of catalytic activity of gold NPs can be theoretically obtained by combination of a few approaches, including the *d*-band model, the jellium model of metal clusters and the Volkenstein`s approach on the role of Fermi level in chemical reactions catalyzed by semiconductors. The microscopic mechanism of the reaction can be explained by using the vibronic theory, in which charge transfer processes play a key role.

II. THE *D*-BAND MODEL

The *d*-band model [23, 24] explains the origin of the chemical bond between a surface of transition metals and a molecule adsorbed onto this surface. According to the model, the adsorbate interacts with the transition metal surface, resulting in two different effects, including a shift and broadening of the adsorbate valence states due the coupling with the *s* states of the metal, and formation of bonding and antibonding states with narrow distributions due to the coupling with the sharp and intense *d*-states of the metal. The strength of the bond is determined by the Fermi level of the metal relative to the energy of the antibonding states of the adsorbate. If the antibonding state is filled by electron transferred from the above laid Fermi level, then the adsorption of the molecule does not occur. If the Fermi level is below the antibonding state, then it is empty. The molecule is adsorbed and forms a strong chemical bond with the surface. The lower it lies with respect to the antibonding state, the stronger the bond is.

It is well known [1] that the ability to accept or donate charge of metal clusters can be tuned by their size. According to the spherical jellium theory of metal clusters [25-27], the ionization potential and the electron affinity depend upon the size of clusters according to the formulas:

$$I(R) = W_b + \alpha \frac{e^2}{4\pi\varepsilon_0 R} + \mathrm{O}(R^{-2}),$$
$$A(R) = W_b - \beta \frac{e^2}{4\pi\varepsilon_0 R} + \mathrm{O}(R^{-2}). \quad (1)$$

Here W_b is the work function of bulk metal, $R = r_s N^{1/3}$ is the radius of the cluster, r_s is the Wigner-Seitz radius, N is the number of atoms in the cluster, α, β are the parameters, which are equal to 3/8 и 5/8, accordingly. Quantum effects implied in terms of higher orders (quadratic and higher) must be accounted for small clusters, N<100 (R<1.5 nm) [25]. Since the Fermi level of gold varies between its ionization potential of 9.2 eV for a single atom and the work function of the bulk, 5.3 eV [1, 27], so their chemical properties can be tuned over a very wide range by variation of the cluster size.

Based on the *d*-band model, it can be assumed that adsorption and desorption of molecules can be tuned by size of metal nanoparticles. Here we should note the effect that the turnover frequency of chemical reactions catalyzed as a function of binding energy of

the reactants onto the catalyst surface yields a volcano-shaped plot [1, 28]. The effect supposes that at low binding energies the reactant is weakly absorbed to form the transition state of the reaction while at high adsorption energies the product does not desorb. Extending these ideas to the CO oxidation by gold NPs, on the basis of the *d*-band model, we can suppose that by decreasing the size of nanoparticles the Fermi level moves down below the antibonding states of the reagents on the surface and the adsorption of CO molecules (and O_2 molecules) takes place (Fig. 1). Until the antibonding states of the product (CO_2 molecules) lie below the Fermi level, their desorption from the surface occurs easily. At further decreasing the size, the number of adsorbed molecules increases and desorption of the products continues to take place until the energy of the Fermi level goes below the antibonding states of the product. The further size decreasing leads to the impairment of desorption of the products. So there is an optimal size range of nanoparticles, when a compromise between adsorption of reagents and desorption of products is reached. For gold nanoparticles, it is obvious from the experiments that the optimal size range is between 1–5 nm. The presented scheme of the reaction can be realized by the assumption that the antibonding states of CO_2 molecules on the surface of the gold nanoparticle lie below the antibonding states of the reagents (CO, O_2) adsorbed, which means that the interaction of the products with the surface is weaker than the interaction between the reagents and the surface, which should be a challenge for experiments and DFT calculations to determine those energy levels, although for bulk gold it is well known that the adsorption of CO_2 molecules is mostly of a physical character [29].

By means of kinetic equations for intermediates of the reaction, those size effects discussed can be quantified. However, as it was mentioned above, the mechanism of the

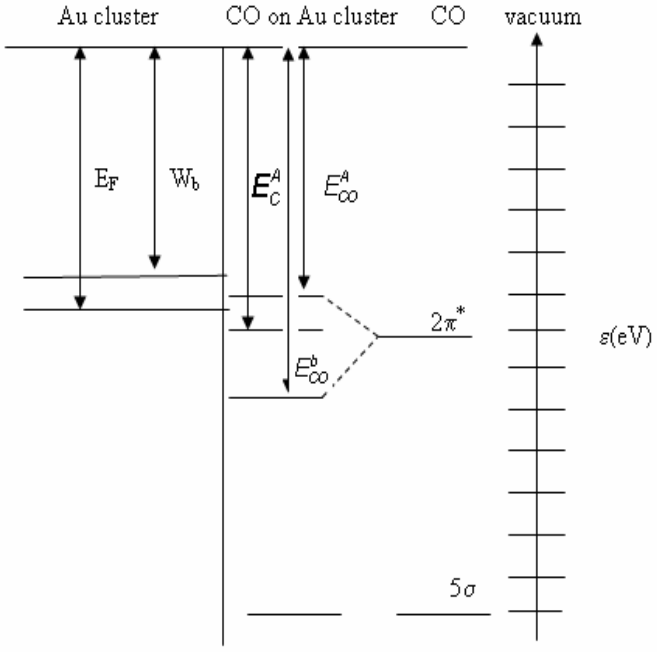


Fig. 1. The scheme of locations of electron energy levels of CO molecules chemically adsorbed on gold nanoparticles relative to the Fermi level of the metal.

reaction is unclear yet, whether the reaction occurs through the adsorption of CO and its reaction with molecules O_2 from air (or supports) or through the absorption of both reagents. We should mention here the classical works of Volkenstein [30] on the role of the Fermi level of semiconducting catalysts in chemical reactions. Through the kinetic equations of chemical reactions, he showed that the chemical reactions could be promoted or inhibited by changing the Fermi level of semiconductors realized by adding dopants. Some chemical reactions can be promoted or inhibited by adding the same dopants but under different conditions (e.g. temperature, pressure). In our previous study [21], the expression for the non-monotonic size dependence of the catalytic activity of gold NPs with respect to CO oxidation was obtained in the frame of kinetic equations for the mechanism of the reaction, when the adsorption of oxygen molecules occurs through dissociation. In that model, the jellium model of metal clusters was taken into account but without consideration of those concepts of the d-band model on the formation of chemical bonds between the adsorbate and the surface. In this study, we would like to derive the expression for a volcano-type size dependence of catalytic activity of gold NPs based on the mechanism of the reaction occurring through adsorption of CO molecules which is energetically favorable [10] by taking into consideration the d-band model. We also suppose that such non-monotonic size dependence should take place for other mechanisms too.

III. A VOLCANO-TYPE SIZE DEPENDENCE

We will consider the mechanism of CO oxidation reaction, in the first step of which adsorption of CO molecules on the surface of gold nanoparticles takes place. They are activated by electrons, which are transferred from the nanoparticle. In the second step, the negatively charged CO molecules react with O_2 molecules from air to form CO_2 molecules being in the activated form, and desorption of neutral products occur. The kinetic equations for those intermediates then take the following forms:

$$\begin{cases} \dfrac{dN_{\mathrm{CO}}^{-}}{dt} = \alpha_{\mathrm{CO}} P_{\mathrm{CO}} \left(1 - s_{\mathrm{CO}} N_{\mathrm{CO}}\right) - \alpha_{\mathrm{O}_2} P_{\mathrm{O}_2} N_{\mathrm{CO}}^{-} + \beta_{\mathrm{O}_2} N_{\mathrm{CO}_2}^{-} \\ \dfrac{dN_{\mathrm{CO}_2}^{-}}{dt} = \alpha_{\mathrm{O}_2} P_{\mathrm{O}_2} N_{\mathrm{CO}}^{-} - \beta_{\mathrm{O}_2} N_{\mathrm{CO}_2}^{-} - \gamma N_{\mathrm{CO}_2}^{0} \end{cases} \tag{2}$$

Here the first term on the right side of the first equation describes adsorption of CO molecules on the metal surface available, where s_{CO} is the effective area of a single chemisorbed molecule CO. The second term takes into account the reaction of those molecules with oxygen molecules, and the third term describes desorption of oxygen molecules. In the second equation, the third term on the right describes desorption of neutral molecules CO_2 from the surface.

At the established equilibrium, we have the following equations:

$$\begin{cases} \alpha_{\mathrm{CO}} P_{\mathrm{CO}} \left(1 - s_{\mathrm{CO}} N_{\mathrm{CO}}\right) = \alpha_{\mathrm{O}_2} P_{\mathrm{O}_2} N_{\mathrm{CO}}^{-} - \beta_{\mathrm{O}_2} N_{\mathrm{CO}_2}^{-} \\ \alpha_{\mathrm{O}_2} P_{\mathrm{O}_2} N_{\mathrm{CO}}^{-} = \beta_{\mathrm{O}_2} N_{\mathrm{CO}_2}^{-} + \gamma N_{\mathrm{CO}_2}^{0} \end{cases}. \tag{3}$$

Assuming $\alpha_{\mathrm{O}_2} P_{\mathrm{O}_2} N_{\mathrm{CO}}^{-} >> \beta_{\mathrm{O}_2} N_{\mathrm{CO}_2}^{-}$, $N_{\mathrm{CO}}^{-} = \eta_{\mathrm{CO}}^{-} N_{\mathrm{CO}}$, $N_{\mathrm{CO}}^{-} = 1 \Big/ \left(\dfrac{\alpha_{\mathrm{O}_2}}{\alpha_{\mathrm{CO}}} \dfrac{p_{\mathrm{O}_2}}{p_{\mathrm{CO}}} + \dfrac{s_{\mathrm{CO}}}{\eta_{\mathrm{CO}}^{-}} \right)$,

we can obtain the following formula for the reaction rate:

$$g = \gamma N^0_{CO_2} = \frac{\alpha_{O_2} p_{O_2}}{\left[\frac{\beta_{O_2}}{\gamma}\frac{\eta^-_{CO_2}}{\eta^0_{CO_2}} + 1\right]} \frac{1}{\left[\frac{\alpha_{O_2}}{\alpha_{CO}}\frac{p_{O_2}}{p_{CO}} + \frac{s_{CO}}{\eta^-_{CO}}\right]}. \quad (4)$$

Here η^-_{CO}, $\eta^-_{CO_2}$ and $\eta^0_{CO_2}$ are the fractions of molecules (CO and CO_2) in negatively charged and neutral states. From the application of the *d*-band model discussed above, we can define those fractions from the difference of antibonding states of adsorbed molecules with respect to the Fermi level of gold nanoparticles E_f according to the following expressions taking into account the formula (1)

$$\eta^-_{CO} = \frac{N^-_{CO}}{N^-_{CO} + N^0_{CO}} = \frac{1}{1 + e^{\left(E^A_{CO-Au} - E_f\right)/kT}} = \frac{1}{1 + e^{\left(E^A_{CO-Au} - \left(W + \alpha e^2/R - E_{sup}\right)\right)/kT}}$$
$$\frac{\eta^-_{CO_2}}{\eta^0_{CO_2}} = \frac{N^-_{CO_2}}{N^0_{CO_2}} = e^{\left(E_f - E^A_{CO_2-Au}\right)/kT} = e^{\left(W + \alpha e^2/R - E_{sup} - E^A_{CO_2-Au}\right)/kT} \quad (5)$$

Here $E^A_{CO\text{-}Au}$ and $E^A_{CO_2\text{-}Au}$ are the antibonding states of CO and CO_2 on the surface of the nanoparticle, respectively, E_{sup} is the term responsible for the contribution of supports to the energy of the Fermi level.

The analysis of the expressions (4) and (5) shows that with decreasing the size of nanoparticles, the rate of the reaction $g(R)$ increases since the corresponding Fermi level goes down below the antibonding states of CO molecules and adsorption becomes stronger, which leads to the increase of the fraction of activated CO molecules. If the size decreases further so the Fermi level passes and goes down below the antibonding states of CO_2 molecules, then desorption becomes difficult, and the reaction rate decreases. So we have two regions in the dependence (Fig. 2). The region A is defined by adsorption of the reagents, while the region B is conditioned by desorption of the products. The role of supports is taken into account by the term E_{sup}, which implies that reducible supports which lowers the Fermi level contribute to the adsorption of molecules while oxidizing supports which raise the Fermi level improve the desorption of the products. This agrees well with the experimental results on reducible supports [11, 14, 16].

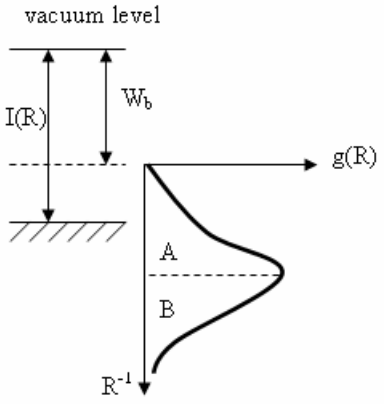


Fig. 2. A Volcano-shaped size dependence of the reaction rate.

IV. THE VIBRONIC THEORY

The microscopic mechanism of activation of reagents in CO oxidation reaction can be explained by using the vibronic theory [22, 31]. According to the theory [31], when the molecule is activated by a catalyst due to their interaction, electronic population of its molecular orbitals changes resulting in electronic redistribution and decompensation of orbital distorting forces and force constants. For the reaction occurring along the normal coordinate Q, changes in vibronic constants will alter the potential surface and the activation energy (D):

$$\Delta D = FQ_D + 3D(\Delta K / K)\left[1 + \Delta K / K + \frac{1}{3}(\Delta K / K)^2\right]. \quad (6)$$

Here F is the distorting force, Q_D is the distance between minimum and maximum points of the potential curve, ΔK is the change of the force constant. Taking into consideration two orbitals of the CO molecule, HOMO 5σ and LUMO 2π, which undergo major charge changes of Δq_1 and Δq_2, respectively, the distorting force and the force constants are calculated by the following expressions:

$$\begin{aligned} F &= f^{(1)}\Delta q_1 + f^{(2)}\Delta q_2 \\ \Delta K &= k^{(1)}\Delta q_1 + k^{(2)}\Delta q_2 \end{aligned}. \quad (7)$$

The coefficients in these expressions, f and k, are constants specific for the CO molecule [31]. From the expressions (7), it is clearly seen, that the negative force, F, weakening the bond and decreasing the activation energy and the negative force constant, ΔK, making the curvature of the barrier gentler, will have higher values for higher positive values of Δq_1 and Δq_2. In terms of the catalyst, this means that its influence will be stronger if its π-donor properties are stronger and its σ-acceptor properties are weaker, which are defined by the Fermi level of the catalyst.

In the previous work [22], we showed that the activation of CO molecules adsorbed on the surface of the nanoparticle toward the oxidation reaction was conditioned by the location of the Fermi level of the nanoparticle with respect to the antibonding states of the adsorbate. If the Fermi level is above the antibonding states, then adsorbtion will not take place. If the Fermi level is below the antibonding states, then adsorption takes place, which results to the transfer of the electron from the Fermi level to the bonding state of the adsorbed molecule. Thus the fraction of charge transferred depends upon the relative location of the Fermi level with respect to the bonding states of CO molecule rather than to the antibonding states as we supposed before [22]. The fraction of charge transferring from the Fermi level of the nanoparticle to the bonding states of 2π LUMO ($E^b_{\text{CO-Au}}$) of the CO molecule is defined by the expression

$$\Delta q_2 = \frac{1}{1 + e^{-(E^b_{\text{CO-Au}} - E_f)/kT}}. \quad (8)$$

The fraction of the charge transferring from the HOMO of the CO molecule (Δq_1) to the nanoparticle is almost zero. We can neglect it in the expressions (7) compared to the second term. We also suppose that on the size range of 1–5 nm, the charge fraction transfer Δq_2 is equal to 1, and its size dependence is weak.

V. CONCLUSION

In summary, we analyzed the volcano shaped plot of the dependence of CO oxidation rate on the size of gold nanocatalysts in the frame of kinetic equations of the reaction for the mechanism, when the reaction occurs through the adsorption of CO molecules reacting with free oxygen molecules. The expression for the dependence has been obtained based on the *d*-band model of formation of the chemical bond between the adsorbate and the metal surface by taking into account the jellium model for spherical metal clusters. According to the model, at the beginning of decreasing the nanoparticle`s size the reaction rate increases due to the enhanced adsorption of the reagents and then decreases due to the impaired desorption of the products. The reducible and oxidizing

supports can contribute to the reaction rate by lowering or raising the Fermi level of the metal clusters, respectively. It is supposed that a volcano-type of size dependence of reaction rate can be also obtained for other mechanisms of the reaction. The origin of the activation of adsorbed reagents by catalysts can be explained in the frame of vibronic theory.

To verify the model results presented, the energy levels of the chemical bond formed between CO_2 molecules and gold nanoparticles should be determined experimentally or by DFT calculations. The presented model has been developed for spherical clusters, but we suppose that it can be applied for other particles (for example, ellipsoid or hemisphere particles) with different coefficients in the expression for the ionization potential.

REFERENCES

1. E. Roduner, Chem. Soc. Rev. **35**, 583 (2006).
2. G.J. Hutchings and M. Haruta, Appl.Catal. A **291**, 2 (2005).
3. M. Haruta, Nature **437**, 1098 (2005).
4. M. Haruta, et al., Chem. Lett. **16**, 405 (1987).
5. M. Valden, X. Lai, D.W. Goodman, Science **281**,1647 (1998).
6. M. Valden, S. Pak, X. Lai, and D.W. Goodman, Catal. Lett. **56**, 7 (1998).
7. M. Haruta, Stud. Surf. Sci. Catal. **110**, 123 (1997).
8. N. Lopez, T.V.W. Janssens, B.S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, and J.K. Nørskov, J. Catal. **223**, 232 (2004).
9. B. Hammer, J.K. Nørskov, Nature **376**, 2238 (1995).
10. J. Kleis, J. Greeley, N.A. Romero, et al., Catal. Lett. **141**,1067 (2011).
11. V.W. Janssens Ton, B.S. Clausen, B. Hvolbæk, et al., Top Catal. **44**(1), 15 (2007).
12. S. Schimpf, M. Lucas, C. Mohr, U. Rodemerck, A. Bruckner, J. Radnik, H. Hofmeister, and P. Claus, Catal. Today **72**, 63 (2002).
13. S.N. Rashkeev, A.R. Lupini, S.H. Overbury, et al., Phys. Rev. B **76**(3), 035438 (2007).
14. U. Landman, B. Yoon, C. Zhang, et al., Top Catal. **44**, 145 (2007).
15. M. Arenz, U. Landman, U. Heiz, Chem. Phys. Chem. **7**, 1871 (2006).
16. M. Chen, D.W. Goodman, Acc. Chem. Res. **39**, 739 (2006).
17. S.M. Kim, H. Lee, K.C. Goddeti, et al., J. Phys. Chem. C **119**(28), 16020 (2015).
18. J.Y. Park, L.R. Baker, G.A. Somorjai, Chem. Rev. **115**(8), 2781 (2015).
19. S.M. Kim, H. Lee, K.C. Goddeti, et al., J. Phys. Chem. C **119**(28), 16020 (2015).
20. J.Y. Park, L.R. Baker, G.A. Somorjai, Chem. Rev. **115**(8), 2781 (2015).
21. N. Turaeva, M. Preuss, Cat. Com. **65**, 30 (2015).
22. N. Turaeva, H. Krueger, Catal. Lett. **147**, 2100 (2017).
23. B. Hammer, J.K. Nørskov, Advances in Catalysis **45**, 71 (2000).
24. J.K. Norskov, F. Abild-Pedersen, F. Studt, T. Bligaard, PNAS **108**, 937 (2011).
25. M. Brack, Rev. Modern. Phys. **65**(3), 677 (1993).
26. J. Perdew, Phys. Rev. B **37**(11), 6175 (1988).
27. M.D. Scanlon, P. Peljo, M.A. Mendez, et al., Nanoparticles Chem. Sci. **6**, 2705 (2015).
28. C.J.H. Jacobsen, S. Dahl, B.S. Clausen, S. Bahn, A. Logadottir, and J.K. Nørskov, J. Am. Chem. Soc. **123**, 8404 (2001).
29. G. Zhang, C.B. Musgrave, J. Phys. Chem. A **111**, 1554 (2007).
30. Th. Volkenstein. The electron theory of catalysis on semiconductors (McMillan, New York, 1963).
31. I.B. Bersuker, Chem. Phys. **31**, 85 (1978).