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Distribution of active site types on Au nanoparticles with different structures: study of thermal dependence

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Abstract

For gold nanoparticles dependencies of low-coordinated atoms count and areas of different faces from nanoparticle size, shape and structure and temperature have been studied. The following recommendations for catalyst developers are proposed: for catalysis of reactions that occur on (111) face icosahedral nanoparticles smaller than 400 atoms must be preferred; reaction that occur on (100) and (110) faces and near low-coordinated atoms, should be better catalyzed by FCC nanoparticles; it should be taken into account, that temperature growth decreases amount of atoms on (111) and (110) faces, and, increases number of low-coordinated atoms and an area of (100) faces.

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Keywords: gold nanoparticles, Monte Carlo method, active sites, low-coordinated atoms

Nomenclature

FCC	face-centered cubic
5fs	five-fold symmetry

1. Introduction

Almost all industrials chemical processes involve catalysts. Oil and gas refinery industry are no exception — catalysts are widely employed in cracking and reforming processes. Nowadays many reactions are catalysed by

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metals, including noble ones. Omnipresence of metallic catalysis is due to a huge diversity of metallic nanoparticles chemical properties that can be varied by controlling nanoparticle's size, shape and structure. Active study of metallic nanoparticles was initiated in 1987 by seminal paper of Haruta et al [1]: for a long time before the gold was considered as an inert metal, but they demonstrated that small enough (less than 5 nm) Au nanoparticles are a very effective catalyst. Since then numerous studies of metallic nanoparticles have been conducted in order to discover new catalytic processes [2] and to explane such a dramatic difference between chemical processes of bulk gold and gold nanoparticles [3-8]. Understanding key factors that influence on interactions between reagents and nanoparticles paves the way to development of novel highly active and selective catalysts. Numerous reasons of high nanoparticles catalytic activity have been suggested: quantum size effects [9], charge transfer between nanoparticles and support [10,11], spillover effects [12-14], oxidation effects [15], and an influence of low-coordinated atoms on nanoparticle's surface [16,17]. Experimental and computational studies give evidences that shape and structure of nanoparticles, including presence and amount of low-coordinated atoms, are crucial factors for chemical properties of nanoparticles, including a very important reaction of hydrocarbons processing - the Fischer–Tropsch synthesis [18-22]. The theoretical insight behind these observations is an assumption that active sites of different chemical reactions are metal atoms with specific coordination numbers.

In this study we have analyzed variations of low-coordinated atoms count with changes of nanoparticle’s size, shape and structure and its temperature dependence.

2. Methodology and computation details

Earlier we have obtained configurations of Au nanoparticles that correspond to putative energy minima of face-centered cubic (FCC) and five-fold symmetry (5fs) structures [23]. In the present study, we computed the number of surface atoms with different coordination numbers for nanoparticles of a size range from 1.7 to 4.6 nm (from 140 to 3000 atoms, with 80 atom step). The size range selection was based on Refs [24-28] that revealed that Au nanoparticles from 2 to 4 nm show the highest catalytic activity.

Temperature dependence of coordination numbers distribution was studied on 2620 atoms nanoparticle. The temperature range was selected to be from 300K to 1300K (melting temperature of bulk gold is 1337 K). Computations were conducted with Monte Carlo method. Interactions between gold atoms were computed with empirical many-body Quantum Sutton-Chen potential [29]. Parameters of the potential were fitted [30] to cohesive energy and surface energies of different faces at the expense of lower precision of elastic constants. Nanoparticle shape is largely determined by its surface energy hence this parameterization tradeoff was considered suitable for aims of this study.

3. Results and discussion

To analyze the dependence of atom coordination number distribution on nanoparticle size, we have used the stable configurations from paper [23]. Fig. 1 shows examples of FCC and 5fs structures with atoms colored according to their coordination numbers.

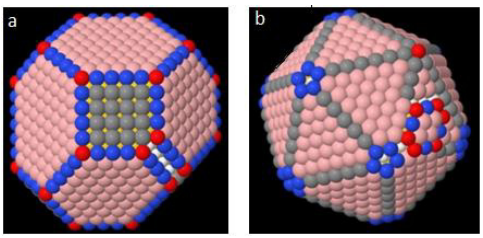

Fig. 1. Example of gold nanoparticles: (a) cuboctahedral nanoparticle with FCC structure, (b) icosahedral nanoparticle with 5fs structure. Color coding of atoms: pink - atoms with coordination number 9, grey - atoms with coordination number 8, blue - atoms with coordination number 7, red - atoms with coordination number 6 or less.

The largest part of the surface is constituted of atoms with coordination number 9 (pink atoms in Fig. 1), that correspond to (111)-FCC faces, for both FCC and 5fs structure motifs. The amount of atoms of this kind is roughly the same for nanoparticles of both motifs larger than 1000 atoms (Fig. 2).

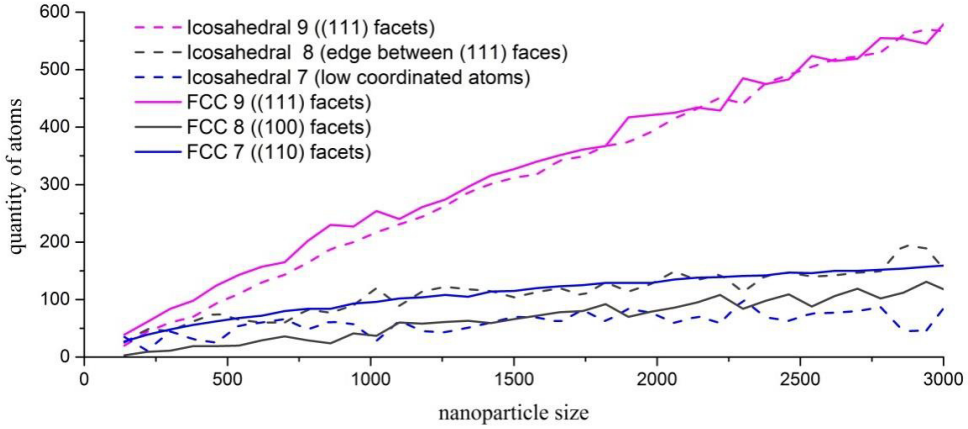

Fig. 2. Dependency of face sizes (in atoms) on nanoparticles size.

Atoms with coordination number 8 (gray atoms in Fig 1.) correspond to (100) faces of FCC structure and to the edges between (111) faces of 5fs structures. Amount of atoms of this kind is smaller for FCC motif (Fig. 2) and grows with roughly the same speed for the whole size range considered here. Nevertheless, one may suppose that for significantly large sizes, the amount of atoms of this kind in FCC structure will exceed the 5fs motif, because surface area grows faster than edges length. But this reasonable suggestion is of a little practical impact – 5fs structure is not stable for large nanoparticles.

Atoms with coordination number 7 are coded blue color in Fig 1. In FCC nanoparticles these atoms correspond to the face (110), that occasionally appears between (111) and (100) faces (including both types of edges – (100)-(111) and (111)-(111)). For FCC structure the amount of such atoms is higher than amount of atoms with coordination number 7, at least for the size range considered in this study. In nanoparticles with 5fs structure atoms with coordination number 7 correspond to chamfered vertices of the icosahedral shape, and to the steps of growing islands on the faces. For 5fs structure, opposite to FCC one, the number of such atoms is smaller than the number of atoms with coordination number 8 in the considered nanoparticles size range.

Atoms with coordination numbers 10 and 11 constitute from 0% to 3% of the surface and their amount barely depends on nanoparticle size. For FCC nanoparticles its average count is 1.73 atoms, for 5fs it is 17.43 atoms. These atoms usually correspond to defect surroundings or to the second layer of the (110) faces.

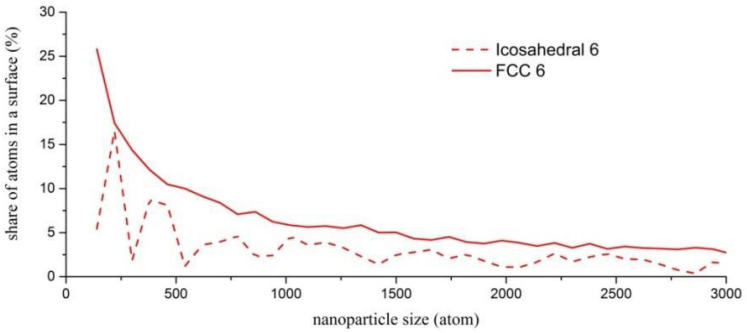

Fig. 3 Dependency of low-coordinated atoms number on nanoparticles size.

Atoms with less than 6 nearest neighbors (red atoms in Fig. 1) are of a special interest to catalysis because of their ability to adjust to adsorbed chemical species and to form interesting transition complexes. They appear as vertices of nanoparticles themselves and of islands on nanoparticle's faces and near surface defects. Fraction of such atoms in overall surface decreases with nanoparticle growth. For icosahedral nanoparticles (5fs structure) this fraction is smaller than for cuboctahedral ones (FCC structure) for all sizes and becomes even smaller in a vicinity of sizes near "magic numbers" of atoms (147, 309, 561, 923, 1415, 2057, 2869) that tend to form shapes with complete external atomic shells (see Fig 3 for plot).

In Monte Carlo studies of temperature dependence of coordination number distribution, for each temperature step 50000 Monte Carlo steps were used for relaxation and the next 50000 Monte Carlo steps were used for averaging measured quantities. For further averaging, 32 independent simulations were conducted.

The obtained temperature dependencies have a definite trend with small non-systematic fluctuations from it. For all considered coordination numbers, the amounts of corresponding atoms change linearly with temperature and are well described by the slope coefficients – k.

Overall square of (111) faces (defined by amount of atoms with coordination number 9) decreases with temperature growth for both structure motifs with the same speed, in both cases characterized by the slope coefficient k_9 = -0.003 (see Fig.4 for plots). Negative k for (111) face is expected from the common physical intuition – this face has the lowest surface energy, hence raise of the system energy caused by temperature growth is reflected by transformation of low-energy faces to higher-energy ones.

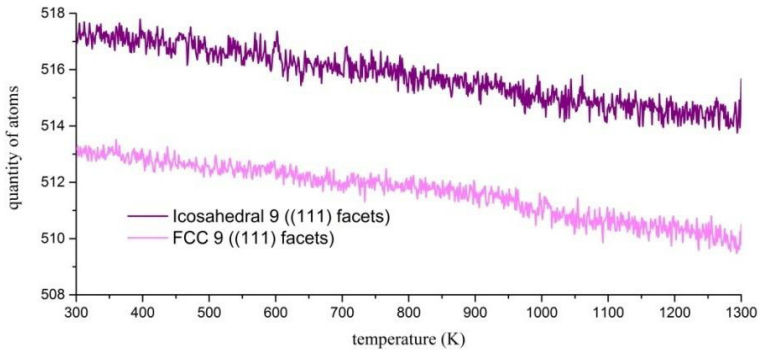

Fig. 4. Dependency of amount of atoms with coordination number 9 on temperature.

Amount of atoms with coordination numbers 8 and 7 shows dissymmetric trends, i.e. slope coefficients with opposite signs: for icosahedral (5fs) motif $k_{5fs,8} = k_{5fs,7} = 0.009$, for FCC structure $k_{FCC,8} = k_{FCC,7} = 0.006$ (see Fig. 5 for plots).

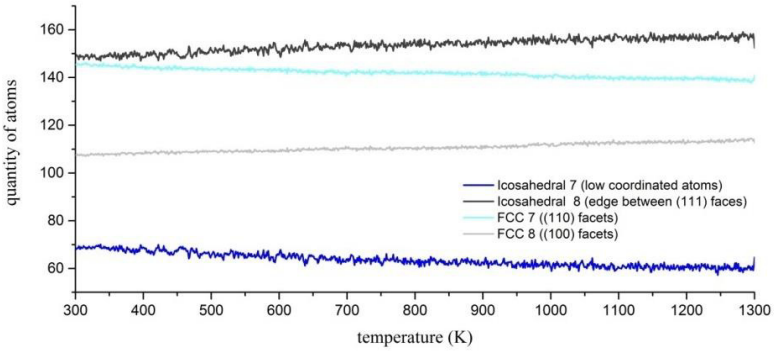

Fig. 5. Dependency of atoms amount with coordination numbers 7 and 8 on temperature.

It is interesting, that for both structures $k_8 > 0$ and $k_7 < 0$. It contradicts the common physical intuition, because (100) faces that correspond to coordination number 8, have lower energy, than (110). One expects that area of high-energy faces grows faster than an area of low-energy ones, but it is not the case as our computations show.

Amount of atoms with coordination number 6 and less (low-coordinated atoms) grows with rise of temperature for both structure motifs. For icosahedral shape $k_{5fs,6} = 0.004$, for cuboctahedral shape $_{kFCC,6} = 0.003$. Although 5fs structure shows faster growth of low-coordinated atoms, FCC structure still possess significantly large number of them up to the melting temperature.

4. Conclusion

From the obtained results several recommendations for catalysis development can be derived.

To catalyze reactions that occur on (111) face of gold crystals, icosahedral nanoparticle with 5fs structure are more preferential than nanoparticles with FCC crystalline structure. According to the study [23], this icosahedral gold nanopaticles are less stable that FCC ones, but energy difference is small for sizes up to 400 atoms, hence icosahedral configurations despite being metastable can persist for a long time. So for catalysis of reaction on (111) face of gold, icosahedral nanoparticles smaller than 400 atoms should be used.

Reaction that occurs on (100) and (110) faces and near low-coordinated atoms, should be better catalyzed by FCC nanoparticles, that posses more atoms of these types.

Catalyst developers should note that temperature growth decreases amount of atoms on (111) and (110) faces, and, contrary, increases number of low-coordinated atoms and, surprisingly, an area of (100) faces.

Acknowledgements

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References

[1] M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, Gold catalysts prepared by coprecipitation for low-temperature oxidation of hydrogen and of carbon monoxide, J. Catal. 115 (1989) 301-309.

[2] J. Gong, Structure and surface chemistry of gold-based model catalysts, Chem. Rev. 112.5 (2011) 2987-3054.

[3] M.D. Hughes, Y.J. Xu, P. Jenkins, P. McMorn, P. Landon, D.I. Enache, A.F. Carley, G.A. Attard, G.J. Hutcgings, F. King, E.H. Stitt, P. Johnston, K. Griffin, C.J. Kiely, Tunable gold catalysts for selective hydrocarbon oxidation under mild conditions, Nature 437. 7062 (2005) 1132-1135.

[4] B. Hvolbaek, T.V.W. Janssens, B.S. Clausen, H. Falsig, C.H. Christensen, J.K. Norskov, Catalytic activity of Au nanoparticles, Nano Today 2.4 (2007) 14-18.

[5] B.Y. Wang, M.X. Liu, Y.T. Wang, X.S. Chen, Structures and energetics of silver and gold nanoparticles, J. Phys. Chem. 115.23 (2011) 11374-11381.

[6] A.J. Logsdail, Z.Y. Li, R.L. Johnston, Faceting preferences for Au N and Pd N nanoclusters with high-symmetry motifs, Phys. Chem. Chem. Phys. 15.21 (2013) 8392-8400

[7] V. Chaban, Annealing relaxation of ultrasmall gold nanostructures, Chem. Phys. Lett. 618 (2015) 46-50.

[8] S. Ali, V.S. Myasnichenko, E.C. Neyts, Size-dependent strain and surface energies of gold nanoclusters, Phys. Chem. Chem. Phys. 18.2 (2016) 792-800.

[9] M. Valden, X. Lai, D.W. Goodman, Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties, Science 281.5383 (1998) 1647-1650.

[10] D. Ricci, A. Bongiorno, G. Pacchioni, U. Landman, Bonding trends and dimensionality crossover of gold nanoclusters on metal-supported MgO thin films, Phys. Rev. Lett. 97.3 (2006) 036106

[11] J.A. van Bokhoven, C. Louis, J.T. Miller, M. Tromp, O.V. Safonova, P. Glatzel, Activation of Oxygen on Gold/Alumina Catalysts: In Situ High-Energy-Resolution Fluorescence and Time-Resolved X-ray Spectroscopy, Angew. Chem. 118.28 (2006) 4767-4770.

[12] G.C. Bond, D.T. Thompson, Catalysis by gold, Catal. Rev. 41 (3,4) (1999) 319-388.

[13] L.M. Molina, B. Hammer, Some recent theoretical advances in the understanding of the catalytic activity of Au, Appl. Catal. A 291.1 (2005) 21-31.

[14] H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, Size-specific catalytic activity of polymer-stabilized gold nanoclusters for aerobic alcohol oxidation in water, J. Am. Chem. Soc. 127.26 (2005) 9374-9375.

[15] J. Guzman, S. Carrettin, J.C. Fierro-Gonzalez, Y. Hao, B.C. Gates, A. Corma, CO Oxidation Catalyzed by Supported Gold: Cooperation between Gold and Nanocrystalline Rare-Earth Supports Forms Reactive Surface Superoxide and Peroxide Species Angew. Chem. Int. Ed. 44.30 (2005) 4778-4781.
[16] T.V.W. Janssens, B.S. Clausen, B. Hvolbæk, H. Falsig, C.H. Christensen, T. Bligaard, J.K. Nørskov, Insights into the reactivity of supported Au nanoparticles: combining theory and experiments, Top. Catal. 44(1-2) (2007) 15-26.
[17] J. Biener, M.M. Biener, T. Nowitzki, A.V. Hamza, C.M. Friend, V. Zielasek, M. Baumer, On the Role of Oxygen in Stabilizing Low-Coordinated Au Atoms, ChemPhysChem 7.9 (2006) 1906-1908.
[18] B.R. Cuenya, F. Behafarid, Nanocatalysis: size-and shape-dependent chemisorption and catalytic reactivity, Surf. Sci. Rep. 70.2 (2015) 135-187.
[19] R.A. van Santen, M.M. Ghouri, S. Shetty and E. M.H. Hensen, Structure sensitivity of the Fischer–Tropsch reaction; molecular kinetics simulations, Catal. Sci. Technol. 1 (2011) 891-911.
[20] S.G. Shetty, I.M. Ciobîcă, E.J.M. Hensen and R.A. van Santen, Site regeneration in the Fischer–Tropsch synthesis reaction: a synchronized CO dissociation and C–C coupling pathway, Chem. Commun.47 (2011) 9822-9824.
[21] X.-Q. Zhang, R.A. van Santen and E.J. M. Hensen, Carbon-Induced Surface Transformations of Cobalt, ACS Catal. 5 (2015) 596–601.
[22] R. A. van Santen, A.J. Markvoort, I.A.W. Filot, M.M.Ghouria and E.J.M. Hensen, Mechanism and microkinetics of the Fischer–Tropsch reaction, Phys. Chem. Chem. Phys. 15 (2013) 17038-17063.
[23] A.I. Svalova, P.V. Stishenko, The Statistical Modeling of the Platinum Nanoparticles in the Transition Area from the Five-fold Symmetry Structure to the Crystal Lattice, Procedia Engineering 113 (2015) 429-434.
[24] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C.J. Kiely, G.A. Attard, G.J. Hutchings, Oxidation of glycerol using supported gold catalysts, Top. Catal. 27(1-4) (2004) 131-136.
[25] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C.J. Kiely, G.J. Hutchings, Oxidation of glycerol using supported Pt, Pd and Au catalysts, Phys. Chem. Chem. Phys. 5.6 (2003) 1329-1336.
[26] M. Haruta, When gold is not noble: catalysis by nanoparticles, Chem. Record 3.2 (2003) 75-87.
[27] A.S.K. Hashmi, G.J. Hutchings, Gold catalysis. Angew. Chem. Int. Ed. 45 (2006) 7896-7936.
[28] C. Della Pina, E. Falletta, L. Prati, M. Rossi, Selective oxidation using gold, Chem. Soc. Rev. 37 (2008) 2077-2095.
[29] A.P. Sutton, J. Chen, Long-range finnis–sinclair potentials, Philos. Mag. Lett. 61.3 (1990) 139-146.
[30] Y. Kimura, Y. Qi, T. Cagin, W.A. Goddard III, The quantum Sutton–Chen many-body potential for properties of fcc metals, Technical Report, California Institute of Technology (1998)