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Allylic Isomerization of Allylbenzene on Nanosized Gold Particles

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Abstract—Nanosized gold particles immobilized on γ-Al_2O_3 exhibited catalytic activity in the allylic isomerization reaction of allylbenzene. As the size of gold nanoparticles was decreased from 40 to 2 nm, their specific activity per surface gold atom nonmonotonically increased from 0.5 to 110 (mol products) (mol $Au_{surface})^{-1}$ h^{-1}. The particles greater than 40 nm were practically inactive.

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INTRODUCTION

Gold nanoclusters exhibit high catalytic activity and selectivity in a number of processes [1–10]. The oxidation of carbon monoxide on gold nanoparticles is an example of the narrow commercial use of nanosized catalysts [11, 12]. A pronounced size effect manifests itself in oxidation and hydrogenation processes on nanoparticles: metal nanoparticles exhibit a high activity under conditions when the bulk or ultradispersed metal is inactive, and the rate of reaction depends on particle size [7–10].

In this work, we immobilized gold nanoparticles on aluminum oxide using anion adsorption and studied their catalytic activity in the reaction of allylbenzene conversion into 2-methylstyrene (allylic isomerization).

EXPERIMENTAL

Starting Materials

Benzene (Aldrich, 98%) and allylbenzene (Aldrich, 98%) were distilled from sodium in an atmosphere of argon.

IKT-02-6M microspherical γ-Al_2O_3 from AO Katalizator with a specific surface area of 138 m^2/g and a total pore volume of 0.32 cm^3/g was used as a support for nanoparticles. The aluminum oxide was activated by calcination at 350°C for 3 h before use.

To prepare catalysts, $HAuCl_4 \cdot xH_2O$ ("Aurate," TU 6-09-05-1075-89) with a gold content of 49.04 wt %, distilled water, and an aqueous 0.1 M NaOH solution were used.

Preparation of Catalysts

(a) Impregnation with chloroauric acid. To prepare ultradispersed gold particles (50–100 nm) immobilized on γ-Al_2O_3, the support was incipient-wetness impregnated with an aqueous solution of $HAuCl_4$ [13]. In a typical experiment, 1 ml of an aqueous solution of $HAuCl_4$ was added to 3 g of γ-Al_2O_3. The gold concentration in solution was varied from 0.152 to 1.52 mol/l, which corresponds to the theoretical weight concentrations of gold on the support from 1 to 10%. After the impregnation, the samples were dried at room temperature for a day. Then, the samples were calcined at 350°C for 2.5 h to remove adsorbed water and to form zerovalent gold particles. The resulting catalysts were kept in a dry atmosphere of argon.

(b) Impregnation with sodium chloroaurate (anion adsorption method). It is well known [14, 15] that aurate ions from an aqueous solution can either undergo physical adsorption in the pores of Al_2O_3 (mechanism 1)

$$Al_2O_3 + AuCl_4^-(aq) \longrightarrow AuCl_4^-(aq)/Al_2O_3$$

or react with aluminum oxide to form surface complexes (mechanism 2):

$$=Al–OH + AuCl_4^- \longrightarrow =Al–O–AuCl_2 + HCl + Cl^-,$$

$$=Al–OH + Au(Cl)_x(OH)_{4-x}^-$$

$$\longrightarrow =Al–O–Au(Cl)_{x-1}(OH)_{3-x} + H_2O + Cl^-$$

$$(x = 1–3).$$

In the impregnation of the support with chloroauric acid, the adsorption of aurate ions occurred in accordance with mechanism 1. After the calcination of a sample containing physically adsorbed aurate ions, the gold precursor aggregation occurred both on the surface and in the pore volume to result in the formation of ultradispersed metal particles, which exhibit low catalytic activity [11, 15]. If the support was impregnated with sodium chloroaurate in an alkaline medium, trivalent gold complexes were formed on the surface of aluminum oxide (mechanism 2). Only surface aggregation occurred in the calcination of these supported complexes, and nanometer-sized particles were formed [15, 16]. The most complete adsorption of the metal as surface complexes was reached at a maximum concentration of free hydroxyl groups of the support [14], which took place when the pH of the solution corresponded to the isoelectric point (IEP) of the support. At pH > IEP, surface OH groups were deprotonated, and their concentration decreased to result in a decrease in adsorption. Moreover, the support surface acquired a negative charge in this case; therefore, the electrostatic repulsion $Au(Cl)_x(OH)^-_{4-x}$ ($x = 0$–4) took place. At pH $\ll$ IEP, the protonation of OH groups caused a decrease in the concentration of free hydroxyls, which are required for sorption. The method described is a version of ion exchange; the name *anion adsorption* used in this work points out the fact that the metal is introduced as an anion rather than protic acid into the composition of a catalyst precursor.

In this study, gold nanoparticles (3–30 nm) were immobilized onto γ-Al_2O_3 from an aqueous solution of sodium chloroaurate in accordance with a published procedure [17].

In a typical experiment, 40-ml portions of aqueous $HAuCl_4$ solutions with gold concentrations from 2.66×10^{-4} to 3.80×10^{-2} mol/l were used to prepare catalysts with metal contents from 0.07 to 10 wt %. The solution obtained was neutralized with sodium hydroxide (0.1 M) to pH 7, and the resulting solution was added to a neutral (pH 7) suspension of γ-Al_2O_3 in water (3 g of γ-Al_2O_3 in 60 ml of H_2O) with stirring. Next, stirring was continued for 3 h at 60°C. In the course of stirring, the support acquired a yellow color, the solution became colorless, and the pH of the solution decreased; these facts suggest the adsorption of aurate ions on the support. In the course of the adsorption of aurate ions, the pH of the solution was thoroughly adjusted at a level of 7 because the IEP of γ-Al_2O_3 is equal to 7.0 [17]. For this purpose, new portions of NaOH (0.1 M) were added dropwise if required. To remove gold unimmobilized on the surface and NaCl, the sediment was washed with 2 l of distilled water using a Buchner funnel. To form surface gold nanoparticles, the samples were dried at 25°C for 24 h and calcined at 350°C for 2.5 h. The resulting catalysts were stored in a dry atmosphere of argon.

Determination of Metal Contents

The gold contents of the resulting samples were determined by atomic absorption spectrometry on a Hitachi 180-80 spectrometer. The metal was preliminarily removed from the support by washing with an aqua regia solution (HCl : HNO_3 = 4 : 1). The metal contents of the catalysts varied from 5×10^{-6} to 5×10^{-5} g/l; the error in the determination of gold amounts was no higher than 1%.

Determination of Average Particle Sizes

The X-ray diffraction (XRD) analysis of catalytic systems was performed on a DRON-3M diffractometer using filtered cobalt radiation. The measurements were performed point by point with a scan step of 0.05° and a point exposure from 10 to 50 s over the angle range 38°–48° (2θ scale).

The average size of immobilized particles was evaluated from integral diffraction line widths using the Debye–Scherrer equation

$$D = \frac{0.94\lambda_{Co}}{\beta\cos\theta},$$

where λ_{Co} is the radiation wavelength (0.179 nm), β is the physical line broadening, and θ is the Bragg angle. The strongest reflection with $d = 0.235$ nm was chosen as an analytical reflection for Au (1,1,1). The adequacy of the use of the Debye–Scherrer equation for determining the size of surface gold crystallites on γ-Al_2O_3 was supported by the following facts:

First, the gold nanoparticle size calculated from the Debye–Scherrer equation was practically equal to the average size found by Costello et al. [17], who performed the measurements by high-resolution transmission electron microscopy (TEM). Thus, according to XRD analysis, the average particle diameter in an Au/γ-Al_2O_3 sample (anion adsorption) with a metal content of 1 wt % was 3.4 nm, whereas the range 3–5 nm was given by Costello et al. [17] for an analogous catalyst.

Second, the results of an XRD study of gold particles immobilized on γ-Al_2O_3 from a colloidal solution of Au–Et_3N [2] are consistent with TEM data for the parent sol of Au–Et_3N. According to XRD data, $d_{average}(Au_n) = 3$ nm in the Au/γ-Al_2O_3 catalyst at a metal content of 0.4%, whereas, according to TEM data, particles with $d(Au_n) = 2$–5 nm (distribution center at about 3 nm) were present in the parent colloidal solution.

Determination of Catalytic Activity

The catalytic experiments were performed in sealed evacuated vessels with intense stirring, which provided the independence of the rate of reaction from the rate of stirring. The rate of the reaction was proportional to the total catalyst amount.

The reaction products were analyzed by gas–liquid chromatography (GLC) and gas chromatography–mass spectrometry (GC–MS). A Kristall Lyuks-4000 instru-

Average particle size of gold ($d_{\text{average}}(\text{Au}_n)$) and the fraction of surface Au atoms in the test samples

Entry	Preparation method	Au content, %	$d_{\text{average}}(\text{Au}_n)$, nm	Fraction of surface Au atoms
1	Acid impregnation	10.0	84 ± 1	0.0015 [9]
2	The same	8.0	52 ± 1	0.0023 [24]
3	″	6.5	39 ± 1	0.018 [24]
4	″	1.0	34 ± 1	0.021 [24]
5	Anion adsorption	10.0	27.0 ± 1	0.024 [9]
6	The same	8.0	18.0 ± 1	0.05 [9]
7	″	6.5	15.0 ± 1	0.11 [9]
8	″	5.0	13.0 ± 1	0.16 [9]
9	″	4.0	8.0 ± 1	0.20 [9]
10	″	3.3	7.5 ± 1	0.22 [9]
11	″	2.5	4.0 ± 1	0.35 [9]
12	″	1.0	3.4 ± 1	0.45 [24]
13	″	0.4	2.7 ± 1	0.52 [24]
14	″	0.3	2.5 ± 1	0.57 [24]
15	″	0.07	2.0 ± 1	0.63 [24]

ment with a column 2 m in length and 0.4 mm in diameter packed with an SE-30 phase and a flame-ionization detector was used for the GLC analysis. The GC–MS analysis was performed on a Finnigan MAT112S instrument at an ionizing electron energy of 75 eV using a capillary column 50 m in length and 0.1 mm in diameter (DB-1 phase).

The activity of catalysts in the units of (mol product) (mol $\text{Au}_{\text{surface}})^{-1}$ h^{-1} was determined from the initial rates of isomerization under standard conditions (catalyst weight of 0.1 g; allylbenzene amount of 7.5×10^{-4} mol; solvent (C_6H_6) amount of 5.6×10^{-3} mol).

RESULTS AND DISCUSSION

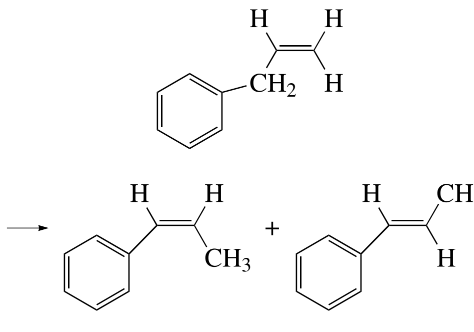
According to published data [13–16], the impregnation of $\gamma\text{-Al}_2\text{O}_3$ with a solution of $HAuCl_4$ followed by thermal reduction to Au^0 resulted in the formation of particles with an average size of 50–100 nm. The black samples of $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ catalysts with gold concentrations from 1 to 10 wt % were prepared by this method.

The $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ systems with immobilized gold nanoparticles from 3 to 30 nm in diameter were formed with the use of the anion adsorption method [13–17]. In this work, catalysts with gold concentrations from 0.07 to 10 wt % were obtained using this method. The samples containing from 0.07 to 5% gold exhibited an intense lilac color. As the metal content was further increased over the range 5–10%, the color gradually changed from lilac to black.

The table summarizes the gold particle sizes in the prepared systems found by XRD analysis. The results of measurements are consistent with published data [16–20]. From the table, it follows that the anion adsorption method allowed us to obtain much smaller particles. It can also be seen that an increase in the metal content resulted in increasing particle size, although the effect manifested itself only slightly with the use of a traditional method of supporting from an acid solution: the average particle size in these samples increased about two times as the gold content was increased from 1 to 10%. A stronger dependence was observed when the catalysts were prepared by the anion adsorption method; in this case, the particle size was approximately proportional to the metal content. A reason for this difference can consist in the lower stability of small nanoclusters, which were obtained by anion impregnation, to aggregation.

Kinetics of the Allylic Isomerization of Allylbenzene

It was found that the rate of the isomerization of allylbenzene depends very strongly on the average metal particle size.



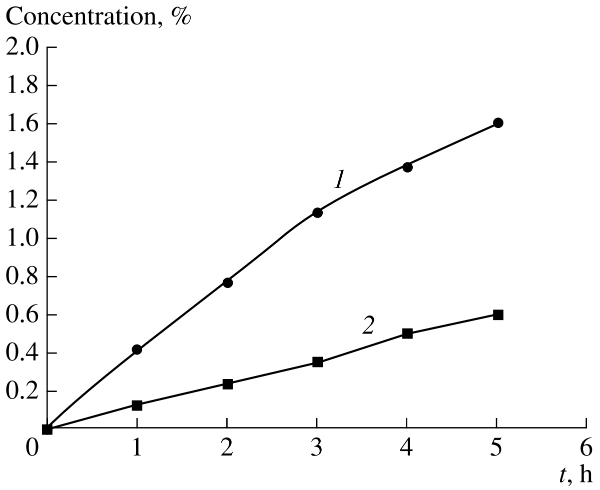


Fig. 1. Kinetic curves of β-methylstyrene formation on ultradispersed gold particles immobilized on aluminum oxide: (*1*) *trans*-β-methylstyrene and (*2*) *cis*-β-methylstyrene. Reaction conditions: $d_{\text{average}}(\text{Au}_n)$ = 34 nm; Au content, 5×10^{-6} mol; allylbenzene content, 7.5×10^{-4} mol; benzene content, 5.6×10^{-3} mol; T = 443 K.

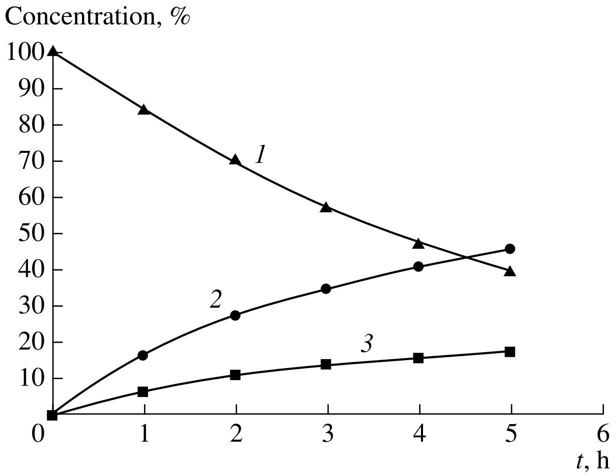


Fig. 2. Kinetic curves of β-methylstyrene formation and allylbenzene consumption on gold nanoparticles immobilized on aluminum oxide: (*1*) PhAll, (*2*) *trans*-β-methylstyrene, and (*3*) *cis*-β-methylstyrene. Reaction conditions: $d_{\text{average}}(\text{Au}_n)$ = 3.4 nm; Au content, 5×10^{-6} mol; PhAll content, 7.5×10^{-4}mol; C_6H_6 content, 5.6×10^{-3} mol; T = 443 K.

On all of the catalysts with average gold particle sizes greater than 40 nm, regardless of catalyst preparation methods, no other products of allylbenzene conversion were detected. As the particle size of the supported metal was decreased to 34 nm or smaller, the rate of isomerization became measurable. Figure 1 shows typical kinetic curves for product formation on gold particles with $d_{\text{average}}(\text{Au}_n)$ = 34 nm.

The experimental curves of allylbenzene consumption were linearized in the coordinates of a first-order reaction ($\ln C$–t, where C is the concentration of PhAll) with the correlation coefficient $R^2 = 0.9939$. The apparent rate constant of the reaction at 443 K found from the $\ln C$–t relation was $k_{\text{app}}(443\text{ K}) = 0.0045 \pm 0.0002\ \text{h}^{-1}$. The apparent activation energy over the temperature range 443–473 K was 98 ± 2 kJ/mol, which is much higher than the activation energy of olefin isomerization on the well-known catalytic systems based on Pt [21].

As mentioned above, a decrease in the average metal particle size was accompanied by a dramatic decrease in the rate of isomerization. Figure 2 shows typical kinetic curves for product formation on the Au/γ-Al_2O_3 catalyst containing 1 wt % gold with $d_{\text{average}}(\text{Au}_n)$ = 3.4 nm. Under these conditions, the order of reaction with respect to allylbenzene was also equal to 1 (in the linearization of experimental data in the $\ln C$–t coordinates, the correlation coefficient R^2 was equal to 0.9996); $k_{\text{app}}(443\text{ K}) = 0.185 \pm 0.002\ \text{h}^{-1}$. The yields of β-methylstyrenes were 48 and 77% in 3 and 8 h, respectively. The activation energy was equal to 30 ± 2 kJ/mol.

Thus, the samples with average particle sizes greater than 40 nm were inactive; at $d_{\text{average}}(\text{Au}_n)$ = 34 nm, their activity became measurable, even if low, whereas it rapidly increased as the size of nanoclusters was further decreased. The size at which the catalytic activity came into play (between 40 and 34 nm) correlates with the point of the onset of change in the melting point of supported gold. According to published data [22, 23], the melting temperature of gold particles up to d_{average} = 37 nm was 1064°C, whereas it began to decrease sharply as the particle size was further decreased. Note that the increase in the activity of gold particles as the particle size was increased is consistent with the previously found change [2] in the heat of adsorption of allylbenzene on gold-containing catalysts. Thus, the heats of adsorption of PhAll on Au/γ-Al_2O_3 with $d_{\text{average}}(\text{Au}_n)$ = 2.7 nm, Au/γ-Al_2O_3 with $d_{\text{average}}(\text{Au}_n)$ = 13 nm, and γ-Al_2O_3 are equal to 71, 55, and 51 kJ/mol, respectively. It is likely that the decrease in the melting temperature, the increase in the heats of adsorption of hydrocarbons, and the appearance of catalytic activity can be considered to result from the appearance of new properties, which are absent from ordinary bulk metal, in gold nanoparticles.

Nature of a Size Effect in the Reaction of Allylbenzene Isomerization on Gold Nanoparticles

To study the dependence of the rate of isomerization on the size of gold particles in more detail, we measured the catalytic activity of these particles from 2 to 37 nm in diameter at 443 K under the standard conditions specified above. The apparent rate of reaction was related to the amount of metal atoms on the surface of gold nanoparticles. The study of the shapes of gold particles immobilized on γ-alumina by impregnation, coprecipitation, and ion exchange demonstrated [15, 22] that they weakly depended on the preparation procedure at gold contents higher than 0.4 wt %, and they can be adequately approximated by a spherical model [22]. For this model, there are ratios between the numbers of surface and bulk atoms [9, 24]. These ratios for gold particles with $d_{\text{average}}(\text{Au}_n)$ from 4 to 30 nm were found using electron-microscopic data and a computer simulation of the surface structure with consideration for particle shapes [9]. For particles with $d_{\text{average}}(\text{Au}_n) <$ 4 nm, we used calculated ratios [24] for shell-structure clusters with a dense packing of atoms.

Figure 3 shows the found dependence of the rate of formation of isomerization products on the particle size of gold. Of course, the model used for the geometry of particles is an approximate model; the error in the evaluation of the number of surface atoms can be as high as tens of percent. However, because the size effect observed was very high (to three orders of magnitude or much higher in terms of surface atoms or the total metal amount, respectively), the qualitative conclusions made can be considered reliable.

As can be seen, a comparatively weak increase in the activity occurred in the range of $d_{\text{average}}(\text{Au}_n)$ from 40 to 27 nm (the overall rate of formation of both of the isomers varied from 0.5 to 5.8 mol (mol $\text{Au}_{\text{surface}})^{-1}$ h^{-1}). In the region from 27 to 13 nm, the activity remained almost constant and the rate was equal to 6.3 ± 0.4 mol (mol $\text{Au}_{\text{surface}})^{-1}$ h^{-1}). The higher rate of isomerization on small gold particles could be explained qualitatively by an increase in the specific surface area; however, in this case, the specific activity (per unit metal surface area) would remain constant. In Fig. 3, it can be seen that, indeed, the rate of reaction remained unaffected over a certain range of d_{average}. However, as the particle size decreased from 13 to 2 nm, the rate of the reaction dramatically increased from 6.3 to 110 mol (mol $\text{Au}_{\text{surface}})^{-1}$ h^{-1} and this cannot be explained by only an increase in the specific surface area.

To a first approximation, the shape of the dependence of the activity of gold nanoparticles in the allylic isomerization reaction on particle size can be qualitatively explained by a change in the nature of the surface as the metal particle size was decreased. The dependence of the concentrations of various surface atoms in gold nanoparticles on particle size over the range 1–30 nm was studied [25, 26]. As $d_{\text{average}}(\text{Au}_n)$ was decreased from 13 to 2 nm, the fractions of angular and edge gold atoms dramatically increased (from 1 to 60 and from 20 to 30%, respectively), whereas the fraction of plane atoms decreased (from 79 to 10%). In this region, we observed a dramatic change in the rate of the reaction (Fig. 3). At the same time, the total fraction of angular and edge atoms remained practically unchanged over a range from 27 to 13 nm; here, the rate of the reaction referenced to the number of surface atoms remained almost unchanged. Next, at $d_{\text{average}}(\text{Au}_n)$ above 27 nm, the contribution of angular and edge atoms monotonically decreased and the activity simultaneously decreased. The total fraction of angular and edge atoms on the surface of particles of size 40 nm was equal to 0.03%. If only these atoms can accelerate olefin isomerization, the practical absence of catalytic activity at $d_{\text{average}}(\text{Au}_n) > 40$ nm becomes clear. Data obtained previously [2] suggest that the most effective adsorption of hydrocarbons and the activation of allylbenzene molecules occur at the same sites.

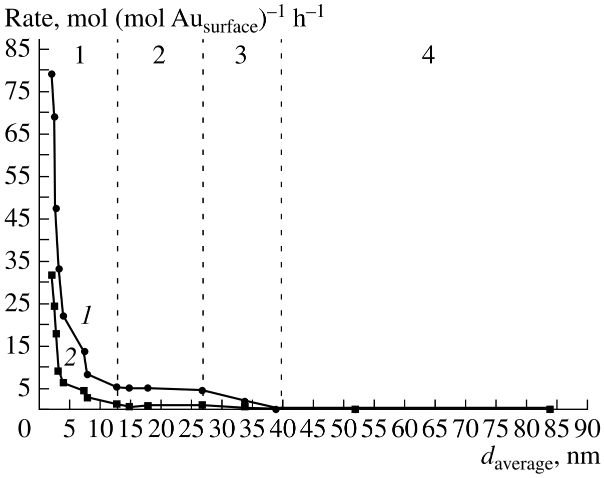


Fig. 3. Dependence of the rate of formation of isomerization products on the particle size of gold: (*1*) *trans*-β-methylstyrene and (*2*) *cis*-β-methylstyrene. Reaction conditions: Au content, 5×10^{-6} mol; PhAll content, 7.5×10^{-4} mol; C_6H_6 content, 5.6×10^{-3} mol; $T = 443$ K.

It is of interest that the size effect influenced not only the activity but also the selectivity of catalysts: the smaller the size of nanoparticles, the lower the ratio between the resulting *trans* and *cis* isomers of β-methylstyrene. Thus, the *trans/cis* ratio was equal to 4.7 ± 0.2 in the region 13–34 nm, whereas it decreased to 2.5 at smaller particle sizes. It is likely that this effect is also related to a change in the surface structure of particles. For example, it is believed that the formation of *cis* or *trans* isomers is more probable in olefin coordination at angular atoms or edges, respectively. It is likely that the size effect with respect to the selectivity of olefin isomerization deserves further investigation in more detail, in particular, with the use of currently available calculation techniques.

Thus, the above study allowed us to draw the following conclusions:

(1) Gold nanoparticles immobilized on aluminum oxide exhibit high catalytic activity in the allylic isomerization reaction of allylbenzene.

(2) The activity of nanoclusters very strongly depends on particle size. Particles more than 40 nm in diameter are practically inactive; particles with an average size from 34 to 13 nm exhibit a comparatively low activity, and a decrease in the size of nanoclusters from 13 to 2 nm is accompanied by a dramatic increase in their activity.

(3) The ratio between the resulting *trans* and *cis* isomers of β-methylstyrene also depends on the average particle size and decreases by a factor of about 2 as the particle size is decreased from 13 to 2 nm.

(4) The experimental data can be qualitatively explained by a change in the relative fractions of atoms of various types on the surface of metal nanoparticles.

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