

Catalytic Activity of Gold-Containing Nanoclusters in Carbon Tetrachloride Addition to Multiple Bonds

S. A. Nikolaev, A. Yu. Vasil'kov, V. V. Smirnov, and L. A. Tyurina

Department of Chemistry, Moscow State University, Moscow, 119991 Russia

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Abstract—Gold nanoparticles immobilized on oxide supports and Au–Ni bimetallic particles catalyze carbon tetrachloride addition to multiple bonds, as is demonstrated by the examples of octene-1 and allylbenzene. The size and catalytic activity of ultrafine particles are governed by the method by which they are prepared. Reaction rate as a function of the total metal content of the catalyst passes through a maximum, whereas the specific activity increases monotonically with decreasing metal content.

INTRODUCTION

Gold is not among the metals commonly used in catalysis. However, interest in gold-containing catalysts has recently increased due to the high selectivity of several processes occurring on these catalysts [1–3]. We have not found any data on the catalytic activity of gold in reactions involving halogenated organic compounds, although these processes are of considerable scientific and practical interest. In particular, one of the incompletely solved problems in the production of some chlorinated organic compounds is that of the utilization of carbon tetrachloride waste [4]. Therefore, expanding the variety of known catalytic systems capable of selectively accelerating reactions involving CCl_4 seems to be a challenging problem.

In this work, we demonstrate, for the first time, that gold can catalyze the addition of CCl_4 to multiple bonds of alkenes and arylalkenes, using octene-1 and allylbenzene as examples. The gold catalysts examined here are ultrafine particles prepared by different methods and supported on silica gel and γ -alumina.

EXPERIMENTAL

Benzene (99.9%), toluene (98%), triethylamine (98%), and allylbenzene (99.9%), all purchased from Aldrich, and octene-1 (98%, Merck) were distilled from sodium. Carbon tetrachloride (97%, reagent grade) was dried and distilled from P_2O_5 . All distilled substances, except olefins, were stored over the molecular sieve 4A (NaA).

Silica gel (Aldrich, $S_{\text{sp}} = 500 \text{ m}^2/\text{g}$) and $\gamma\text{-Al}_2\text{O}_3$ produced at AO Katalizator (IKT-02-6M brand, $S_{\text{sp}} = 138 \text{ m}^2/\text{g}$) were used as supports. Before being loaded with metal, the supports were activated by calcination

for 3 h: SiO_2 was calcined at 500°C , and $\gamma\text{-Al}_2\text{O}_3$ was activated at 350°C .

Nanoclusters and ultrafine particles were immobilized by impregnation [5], anion adsorption [6], or metal vapor synthesis (MVS).

MVS was carried out by condensation of metal vapor with triethylamine [7, 8] and toluene [9, 10] at $77\text{--}80 \text{ K}$, using a procedure that we had earlier developed for the preparation of stable metal colloids. Nanoclusters were immobilized on the support after melting the condensate as described in [9, 10].

In the impregnation and deposition–precipitation methods, gold was supported from an aqueous solution of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ with an Au content of 49.04 wt %. To obtain nanoclusters and ultrafine gold particles on the surface, the catalyst precursor was calcined at 350°C for 3 h.

The gold and nickel contents of samples were determined by atomic absorption spectroscopy on a Hitachi 180-80 spectrometer. The metal was preliminarily washed off the support with a solution of aqua regia ($\text{HCl} : \text{HNO}_3 = 4 : 1$). The sensitivity of this method was 5×10^{-6} to $5 \times 10^{-5} \text{ g/l}$.

Micrographs of Au–toluene, Au– Et_3N , Au–Ni– Et_3N , and Ni– Et_3N organosols were obtained using a JEM-100 (JEOL) microscope with a resolution of 1–2 nm at a magnification factor of 150000. Particle size distribution for each sample was determined by statistical processing of data for 300 particles.

Catalytic tests were carried out in sealed pumped vessels under vigorous stirring, so the reaction rate was not controlled by diffusion.

Products were analyzed by gas–liquid chromatography (GLC) and gas chromatography coupled with mass spectrometry (GC–MS). GLC was carried out on a Kristall-100 chromatograph with a packed column 2000 mm in length and 0.4 mm in diameter (SE-30 phase, flame-ionization detector). GC–MS analysis

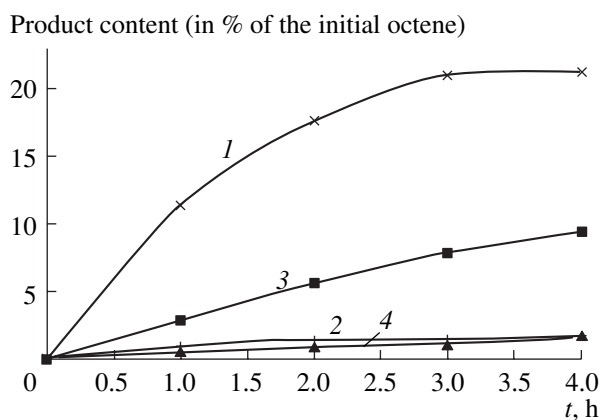


Fig. 1. Accumulation of the products of the $\text{CCl}_4 + \mathbf{1}$ reaction on the $\text{Au}/\text{Al}_2\text{O}_3$ catalyst prepared by the deposition-precipitation technique under standard conditions (Au content is 1.3 wt % (6.6×10^{-6} mol)): (1) first $\text{C}_9\text{H}_{16}\text{Cl}_4$ isomer, (2) second $\text{C}_9\text{H}_{16}\text{Cl}_4$ isomer, (3) first $\text{C}_8\text{H}_{15}\text{Cl}$ isomer, and (4) second $\text{C}_8\text{H}_{15}\text{Cl}$ isomer.

was carried out on a Finnigan MAT112S instrument equipped with a capillary column 50000 mm in length and 0.1 mm in diameter (DB-1 phase) using an ionizing voltage of 75 eV.

The activity of the catalysts was estimated from the initial reaction rate under standard conditions: the amount of catalyst was 0.1 g, metal content ranged from 10^{-5} to 10^{-6} mol, the total volume of the liquid phase was 0.7 ml, the amounts of reactants were 6.4×10^{-4} mol of octene-1 or 7.5×10^{-4} mol of allylbenzene and 5×10^{-3} mol of CCl_4 , temperature was 130°C , and reaction time was 2 h. Apparent activation energy was derived from the slope of the Arrhenius plot of reaction rate between 90 and 130°C .

CATALYTIC PROPERTIES OF ULTRAFINE GOLD PARTICLES PRODUCED BY DIFFERENT METHODS

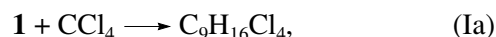
Impregnation

According to published data [5], impregnation of a support with an HAuCl_4 solution followed by thermal reduction of the metal to Au^0 provides ultrafine particles with an average size of 50–100 nm. The average metal content of the catalysts thus obtained was $0.4 \pm 0.1\%$ (pink samples) or $2.0 \pm 0.3\%$ (black samples). SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ were used as supports. It was preliminarily ascertained that no reactions in the CCl_4 -olefin systems occur on these supports, supported HAuCl_4 , or gold(I) chloride (supported as a complex with triphenylphosphine). Ultrafine particles of gold metal obtained by impregnation also did not exhibit any appreciable activity under standard conditions. In none

of the runs did we observe addition (or any other) products.

The Deposition-Precipitation Technique

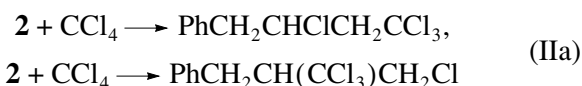
The deposition-precipitation technique [6] was used to prepare catalysts only on aluminum γ -oxide, because silica gel is chemically unstable under the conditions examined. The metal content of the catalyst was varied between 0.07 and 5%. All samples were rich lilac. They showed an appreciable catalytic activity in the addition of CCl_4 to multiple bonds. The selectivity of the reactions was low. In the case of octene-1 (**1**), the addition reaction yielding two isomers with different positions of the Cl and CCl_3 substituents,



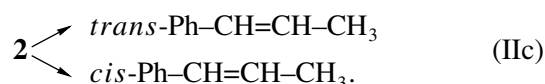
was accompanied by a side substitution reaction (designated (Ib)) yielding 3-chlorooctene-1 (*trans* and *cis* isomers in a 6 : 1 ratio). Apparently, this product resulted from hydrogen elimination from octene-1 by chloroalkyl radicals that had formed through the addition of CCl_3 to the multiple bond followed by interaction between the resulting radical and a second (third, etc.) olefin molecule. In this case, various isomeric products, such as $\text{C}_9\text{H}_{16}\text{C}_3(\text{C}_8\text{H}_{16})_n\text{Cl}$ or $\text{C}_9\text{H}_{16}\text{C}_3(\text{C}_8\text{H}_{16})_n\text{H}$ (where $n = 0, 1, 2$, and so on), must be formed along with 3-chlorooctene-1. These heavy products were not identified. Only compounds with $n = 1$ were qualitatively detected.

As judged from the product accumulation curves (Fig. 1), the addition and substitution reactions are parallel and the ratio of the total yields of addition and substitution products under standard conditions is close to 3 : 1. The activity of the catalyst decreases during the reaction, and octene-1 conversion in 4 h does not exceed 40% in most cases. Addition ceases as soon as 2.5–3 h after the beginning of the reaction, while substitution continues for another several hours (although at a lower rate).

The reaction between CCl_4 and allylbenzene (**2**) in the presence of gold nanoparticles obtained by the deposition-precipitation technique occurs in a somewhat different manner. The selectivity of this reaction is also low: addition to the multiple bond,



is accompanied by a substitution reaction similar to (Ib) (designated (IIb)) and by allylbenzene isomerization



The ratio of the isomers of the addition product is (22–31) : 1, the ratio of the substitution product is

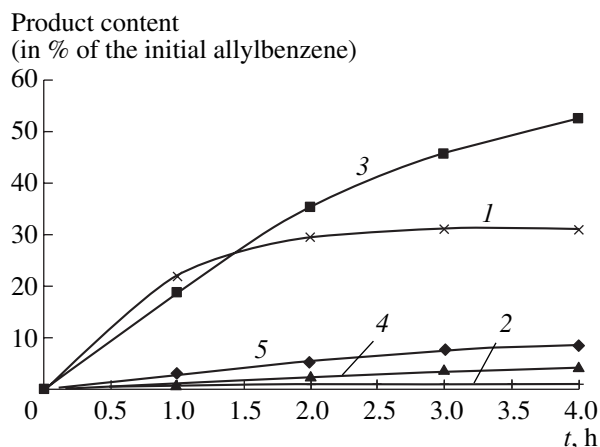


Fig. 2. Accumulation of the products of the $\text{CCl}_4 + 2$ reaction on the $\text{Au}/\text{Al}_2\text{O}_3$ catalyst prepared by the deposition-precipitation technique under standard conditions (Au content is 1.3 wt % (6.6×10^{-6} mol)): (1) $\text{PhCH}_2\text{CHClCH}_2\text{CCl}_3$, (2) $\text{PhCH}_2(\text{CCl}_3)\text{CH}_2\text{Cl}$, (3) first $\text{C}_9\text{H}_9\text{Cl}$ isomer, (4) second $\text{C}_9\text{H}_9\text{Cl}$ isomer, and (5) sum of the *cis* and *trans* isomers of allylbenzene.

(12–16) : 1, and the ratio of the *trans* and *cis* isomers of β -methylstyrene is (3–10) : 1. A specific feature of the reaction involving allylbenzene is that, under standard conditions, addition slows down rapidly and stops after approximately 2 h (the total yield of addition products is $30 \pm 5\%$), whereas the competing substitution process proceeds without a noticeable deceleration for 5–6 h, until **2** is completely consumed. In the early stages of the process, the addition and substitution products are formed in a ratio close to 1 : 1. At the end of the reaction, the yield of substitution products is approximately twice as high as the yield of addition products. It is of interest that isomeric methylstyrenes build up during the reaction and there are no indications of CCl_4 addition to them. Typical curves of compound **2** consumption and product accumulation are presented in Fig. 2.

For a fixed catalyst weight, catalytic activity as a function of metal content passes through a maximum (Fig. 3). Catalytic activity per unit amount of metal (specific activity) increases with decreasing gold content (Fig. 4).

An interesting feature of the process is the rather low apparent activation energy. For example, for a catalyst containing 2.5% Au, the activation energy is 10 ± 1 kcal/mol for the addition of CCl_4 to octene-1 and 12 ± 1 kcal/mol for the addition of CCl_4 to allylbenzene. These values are lower than the values reported for similar reactions on typical initiator catalysts. For instance, the activation energy of CCl_4 addition to octene-1 in the presence of molybdenum complexes with donor ligands is 20 ± 2 kcal/mol [12].

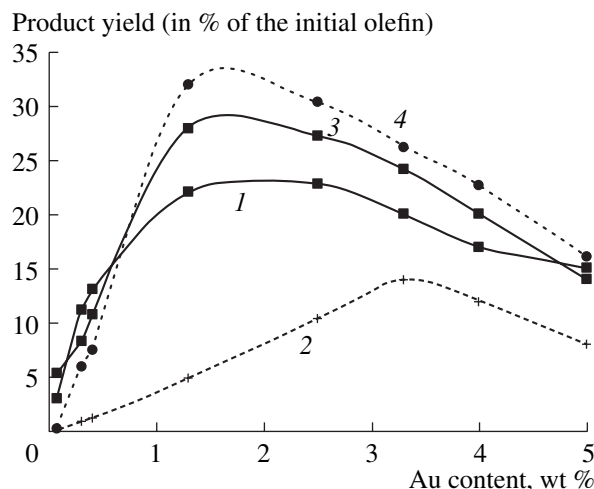


Fig. 3. Activity of the $\text{Au}/\text{Al}_2\text{O}_3$ catalyst versus metal content (standard conditions): (1) $\text{C}_9\text{H}_{16}\text{Cl}_4$, (2) $\text{C}_8\text{H}_{15}\text{Cl}$, (3) $\text{C}_{10}\text{H}_{10}\text{Cl}_4$, and (4) $\text{C}_9\text{H}_9\text{Cl}$.

Metal Vapor Synthesis

It was earlier shown that, in toluene solutions, transition metals form metastable bisarene complexes, whose decomposition produces nanoparticles [9, 10]. When triethylamine is used, colloidal dispersions containing metal nanoparticles form immediately and it is these nanoparticles that are deposited on the oxide surface [7, 8]. Typical transmission electron micrographs of the $\text{Au}-\text{Et}_3\text{N}$ system are shown in Fig. 5, and the particle size distribution in this system is demonstrated in Fig. 6. The distribution function peaks at 5–7 nm, and more than 90% of the particles have a size of 3 to 9 nm. For the toluene dispersion, a broader particle size distri-

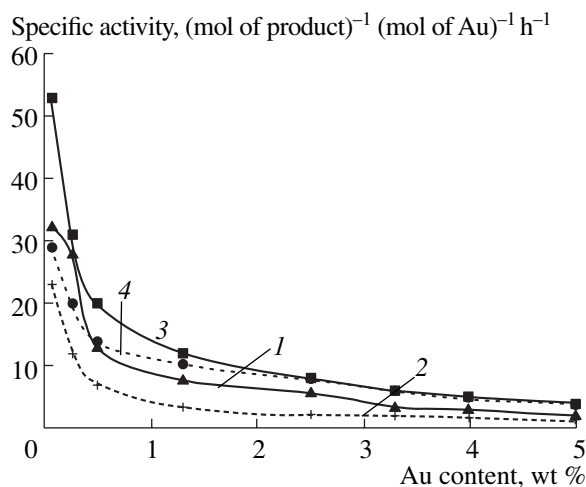


Fig. 4. Specific catalytic activity versus the metal content of $\text{Au}/\text{Al}_2\text{O}_3$ (standard conditions): (1) $\text{C}_9\text{H}_{16}\text{Cl}_4$, (2) $\text{C}_8\text{H}_{15}\text{Cl}$, (3) $\text{C}_{10}\text{H}_{10}\text{Cl}_4$, and (4) $\text{C}_9\text{H}_9\text{Cl}$.

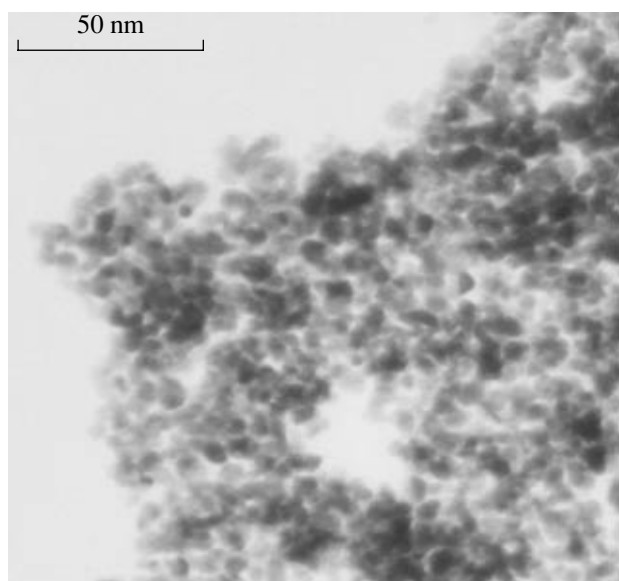


Fig. 5. Micrograph of gold nanoparticles in the Au-Et₃N colloidal system.

bution and larger particles are observed: the histogram has a diffuse maximum at 20–40 nm, and particle size ranges from 6 to 60 nm. A still broader distribution is characteristic of nickel in triethylamine: the maximum occurs at 50 nm, and particle sizes between 15 and 95 nm are detected. Note that the particle size data for nickel compare well with data observed for a wide variety of metals [8], while gold behaves abnormally: its particle size is smaller than the particle size of other transition metals by one order of magnitude. The particle size distribution in the Au–Ni systems is the broadest and is obviously bimodal, with a sharp maximum at 6 nm and a diffuse peak near 45 nm (Fig. 7). This system consists of 2- to 100-nm particles.

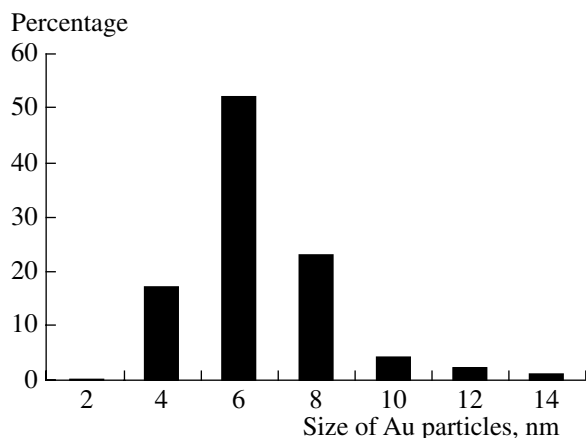


Fig. 6. Size distribution of gold nanoparticles in the Au-Et₃N system.

The decomposition of the colloidal dispersions of Au in toluene, Au or Au + Ni in triethylamine, and Ni in triethylamine in the presence of the support gave, respectively, black, purple, and yellow immobilized systems. The metal content of the catalyst ranged between 0.05 and 0.5 wt %.

Regardless of metal content, the catalysts obtained by metal deposition from toluene and the catalysts containing only Ni are inactive in CCl₄ addition to multiple bonds. On the contrary, the gold-containing catalysts prepared from triethylamine exhibit high activity. The qualitative composition of the products formed on these catalysts differs greatly from that observed for catalysts produced by the deposition–precipitation technique: substitution reactions (Ib) and (IIb) and isomerization (IIc) do not occur at all, and the addition reactions (Ia) and (IIa) show 100% selectivity. Data characterizing the activity of the catalysts examined are presented in the table. Note that catalytic activity can approach 300 (mol of product) (mol of Au)^{–1} h^{–1} in the most favorable cases. This value is close to the activity observed at lower temperatures for colloidal dispersions of active metals in triethylamine produced by MVS without immobilization. For instance, the activity of Cu and Sm colloids in triethylamine in CCl₄ addition to hexene-1 at 80°C is 200 and 50 (mol of product) (mol of metal)^{–1} h^{–1}, respectively [11].

The data presented in the table show that the specific activity of the gold nanoclusters obtained by MVS and of the nanoparticles prepared by the deposition–precipitation technique (Fig. 4) increases with a decrease in the metal content of the catalyst. No synergistic effects were observed for Au–Ni mixed samples.

SPECIFIC FEATURES OF CATALYTIC CCl₄ ADDITION REACTIONS ON GOLD NANOPARTICLES

Under certain conditions, catalysts based on gold nanoparticles exhibit a high activity in CCl₄ addition to

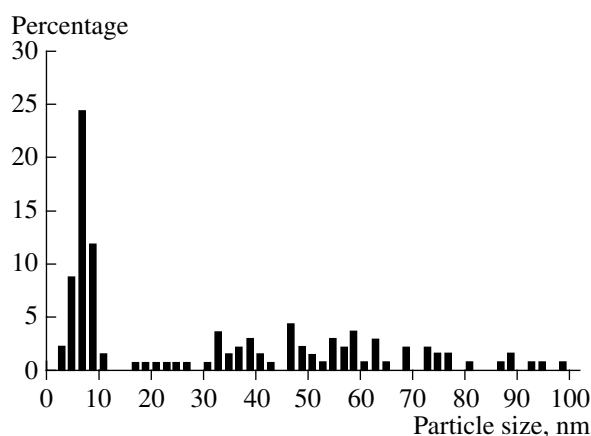
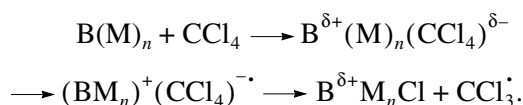


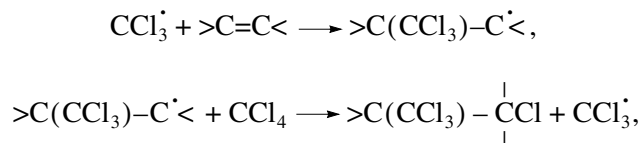
Fig. 7. Size distribution of metal particles in the Au–Ni–Et₃N colloidal system.

multiple bonds of hydrocarbons. Therefore, they may be of use in the conversion of polyhalogenated compounds. The catalytic effect of gold has specific features that are of special significance. For instance, the activity and selectivity of gold catalysts are definitely correlated with the method of preparation and size of the nanoparticles. Impregnation, which yields particles with a linear size of $r \geq 50$ nm, does not afford active catalysts. Such catalysts can be prepared by the deposition-precipitation technique ($r = 3\text{--}30$ nm [6] in this case). The highest activity is shown by the systems prepared from a colloidal dispersion in triethylamine ($r = 4\text{--}14$ nm). These results allow a trivial qualitative explanation: specific surface increases with decreasing particle size. However, it seems that this correlation is not the single or main factor determining catalytic activity. For example, although a colloidal gold dispersion in toluene contains a measurable number of particles with $r < 10$ nm, the activity of the corresponding catalyst is zero. Furthermore, the ratio of particle surface area to particle volume or, what is the same, to particle weight, must be approximately inversely proportional to linear particle size. If the properties of the catalysts were determined only by the surface area, their activity per unit weight would show the same trend. In fact, while the sizes of particles obtained by impregnation, the deposition-precipitation technique, and MVS in triethylamine differ by at most one order of magnitude (for the two MVS variants, this difference is still smaller), the activities of these particles differ by at least 2–3 orders of magnitude (with allowance made for measurement errors at low product concentrations).

It can be assumed that, in MVS involving triethylamine, basic species (B), specifically, adsorbed molecules or fragments of amine molecules remain on the metal surface after catalyst formation. These species favor electron transfer from the metal, and this process, according to [13], is the first step in the generation of active species involved in CCl_4 addition to multiple bonds:



Next, depending on the environment of the reaction center, either radicals pass into the solution to participate in an ordinary chain reaction,



or the process takes place on the catalyst surface (without the formation of free radicals or their escape to the solution). It is apparently the competition between these two pathways that is responsible for the fact that catalysts prepared by anion adsorption and catalysts

Catalytic activity of gold nanoparticles obtained by condensation of gold with triethylamine followed by immobilization on oxide supports

Support	Au content of the catalyst, %	Ni content of the catalyst, %	Activity, $\text{mol mol}^{-1} \text{h}^{-1}$	
			reaction (Ia)	reaction (IIa)
Al_2O_3	0.18	—	162	37
	1.22	—	22	6
	1.32	—	20	6
	0.40	0.30	85	29
	0.87	0.28	42	12
	1.22	0.40	26	10
SiO_2	0.06	—	282	74
	0.80	—	36	11
	1.35	—	20	7
	0.14	0.10	164	90
	0.46	0.30	117	54
	0.49	0.16	75	24

Note: Standard experimental conditions; the accuracy of activity determination is $\pm 10\%$.

synthesized using a triethylamine sol lead to products differing in composition.

The cause of the antibatic dependence of the specific activity of the metal on its content in the sample is worthy of special study. On the one hand, this dependence can be explained by the aggregation of the metal taking place as its amount on the surface increases. On the other hand, similar dependences observed for iron- and copper-containing catalytic systems were considered to arise from the character of intercluster interaction changing with average intercluster distance [14]. We intend to consider this problem in more detail in forthcoming publications.

As a whole, the above results show that systems based on gold nanoparticles can be efficient catalysts for reactions involving carbon tetrachloride and are of obvious interest for researchers developing new methods for the conversion of polyhalogenated hydrocarbons.

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REFERENCES

1. Milone, C., Tropeano, M.L., Gulino, G., and Neri, G., *Chem. Commun.*, 2002, p. 869.

2. Armin, L., Anke, W., and Ferdi, S., *Catal. Lett.*, 2001, vol. 73, nos. 2–4, p. 158.
3. Sárkány, A. and Horvath, A., Beck, *Appl. Catal., A*, 2002, vol. 229, p. 121.
4. Zhanavskiy, L.N. and Aver'yanov, V.N., *Khim. Prom-st.*, 2002, no. 9, p. 1.
5. Bond, G.C., *Catal. Rev.—Sci. Eng.*, 1999, vol. 41, nos. 3–4, p. 339.
6. Costello, C.K., Kung, M.C., and Oh, H.-S., *Appl. Catal., A*, 2002, vol. 232, p. 160.
7. Kondakov, S.E., Smirnov V.V., *Bull. Soc. Chim. Belg.*, 1994, vol. 103, p. 131.
8. Kondakov, S.E., Smirnov, V.V., and Olenin, A.Yu., *Bull. Soc. Chim. Belg.*, 1995, vol. 104, p. 369.
9. Solodovnikov, S.P., Vasil'kov, A.Yu., Olenin, A.Yu., Titova, E.F., and Sergeev, V.A., *Dokl. Akad. Nauk SSSR*, 1990, vol. 310, no. 4, p. 912.
10. Vasil'kov, A.Yu., Olenin, A.Yu., Titova, E.F., and Sergeev, V.A., *J. Colloid Interface Sci.*, 1995, vol. 169, p. 356.
11. Kondakov, S.E., Smirnov, V.V., and Tyurina, L.A., *Dokl. Akad. Nauk SSSR*, 1992, vol. 325, p. 538.
12. Bland, W.J., Davis, R.A., and Durrant, J.L., *J. Organomet. Chem.*, 1985, vol. 280, p. 397.
13. Tarkhanova, I.G., Rostovshchikova, T.N., Kharitonov, D.N., and Smirnov, V.V., *Kinet. Katal.*, 1998, vol. 39, no. 6, p. 882.
14. Rostovshchikova, T.N., Yavsin, D.A., Smirnov, V.V., Kozhevnikov, V.M., and Gurevich, S.A., *Kinet. Katal.*, 2003, vol. 44, no. 4, p. 607.