Adsorption and catalytic conversion of hydrocarbons on nanosized gold particles immobilized on alumina

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Gold and nickel particles immobilized on alumina were prepared by the metal vapor synthesis and anionic adsorption methods. The dispersion of metals was determined by X-ray diffraction and transmission electron microscopy. The activity of nanoparticles, tested in model catalytic reactions of CCl_4 addition to multiple bonds and allyl isomerization of allylbenzene, changes in a wide range (from 1 to 3000 (mole of product) (mole of Au)$^{-1}$ h^{-1}) and is parallel to the chromatographically measured heats of adsorption of the corresponding unsaturated substrates. The heat of adsorption of unsaturated hydrocarbons can serve as a criterion for the efficiency of the gold-containing catalyst in olefin conversion.

Key words: gold, alumina, adsorption of hydrocarbons, catalysis, metal vapor synthesis, anionic adsorption, isomerization, addition, carbon tetrachloride.

Nanosized gold particles possess high catalytic activity and selectivity.[1—11] Gold nanoparticls immobilized on oxide supports are highly active in the addition of carbon tetrachloride to multiple bonds[12] and in the allyl isomerization of olefins.[13] Information on the strength and nature of interaction of nanoparticles with reactants is necessary for an understanding of the mechanisms of isomerization and addition that occur on immobilized gold nanoparticles. Therefore, data on the adsorption of reagents and test molecules of different types are of great interest.

In the present work, the heats of adsorption of carbon tetrachloride, allylbenzene, and oct-1-ene on nanosized particles of gold, nickel, and mixed samples Au + Ni were measured by chromatography. To reveal the contribution of alkyl chains, double bonds, and aromatic fragments of substrate molecules, alkanes and simplest aromatic hydrocarbons were chosen as test substances. The simplest homologue of CCl_4, *viz*, chloroform, was taken to elucidate the contribution of the C—Cl bond to adsorption.

Experimental

Benzene (Aldrich, 98%), allylbenzene (Aldrich, 98%), and oct-1-ene (Merck, 96%) were distilled over sodium. Halosubstituted hydrocarbons, ethanol, alkanes, and triethylamine (all special purity grade, 98%) were used after drying and distillation. All distilled samples, except for olefins, were stored above molecular sieves 4 Å (NaA).

Preparation of catalysts by the anionic adsorption and metal vapor synthesis methods. Immobilized nano- and ultradispersed particles were obtained by anionic adsorption and metal vapor synthesis.[12]

Microspherical γ-Al_2O_3 (IKT-02-6M trade mark, AO Katalizator, Russia) with a specific surface of 138 m^2 g^{-1} was used as the support for nanoparticles. When the catalysts were prepared by anionic adsorption, chloroauric acid hydrate $HAuCl_4 \cdot xH_2O$ (Aurat, TU 6-09-05-1075-89 trade mark) with the weight content of Au 49.04%, distilled water, and a 0.1 *M* solution of NaOH were used. A gold and/or nickel wire (l = 30 mm, d = 1.5 mm) was used as the metal source in the metal vapor synthesis.

Determination of the average particle size by transmission electron microscopy (TEM) and X-ray diffraction analysis. Electronic microphotographs of organosols Au—Et_3N, Au—Ni—Et_3N, and Ni—Et_3N were obtained on a Jem-100 instrument with a resolution ability of 1—2 nm and an amplification of $1.5 \cdot 10^5$ times. In each case, data were processed using the statistical method by 300 particles to determine the particle size distribution.

The X-ray diffraction study of the catalytic systems was carried out on a DRON-3M diffractometer using filtered cobalt radiation with a scan increment of 0.05° and the exposure to the point from 10 to 50 s in the 2θ range from 38 to 48°.

The dispersion of immobilized particles was estimated from the broadening of X-ray diffraction peaks. The size of gold crystallites was determined from the Debye—Scherrer formula. The

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strongest reflection at $d = 0.235$ from the [111] plane of Au was chosen as an analytical reflection.

Determination of the metal content in the catalytic systems. The content of gold and nickel in the samples was determined by the atomic absorption method on a Hitachi 180-80 spectrometer. The metal was preliminarily washed from the support with a solution of concentrated acids ($HCl : HNO_3 = 4 : 1$). The sensitivity of the method was $5 \cdot 10^{-6}$—$5 \cdot 10^{-5}$ g L^{-1}.

Determination of the catalytic activity in model catalytic reactions. Catalytic experiments were carried out in sealed evacuated vessels with vigorous stirring in the kinetic regime of the reaction.

Products were analyzed by the GLC and GC-MS methods. A KristalLyuks-4000 instrument with a packed column ($l = 2$ m, $d = 0.4$ mm, SE-30 phase, flame-ionization detector, nitrogen as carrier gas) was used for GLC. Analysis by GC-MS was carried out on a Finnigan MAT112S instrument with an energy of ionizing electrons of 75 eV using a capillary column ($l = 50$ m, $d = 0.1$ mm, DB-1 phase).

The activity of the catalysts in allylbenzene isomerization ((mole of product) (mole of Au)$^{-1}$ h^{-1}) was determined in standard experiments: the weight of the sample (Au/γ-Al_2O_3) was 0.1 g, the metal amount in the weighed sample was 10^{-5}—10^{-6} mol, the amount of allylbenzene was $7.5 \cdot 10^{-4}$ mol, the amount of benzene was $5.6 \cdot 10^{-3}$ mol, the temperature was 170 °C, and the reaction time was 3 h.

The activity of the catalysts in CCl_4 addition to the multiple bond was determined in standard experiments: the weight of the sample (Au/γ-Al_2O_3) was 0.1 g, the metal amount in the weighed sample was 10^{-5}—10^{-6} mol, the amount of olefin was $7.5 \cdot 10^{-4}$ mol, the amount of CCl_4 was $5.2 \cdot 10^{-3}$ mol, 130 °C, and the reaction time was 2 h.

Chromatographic measurements and determination of the heats of adsorption. Chromatographic measurements were carried out on a Tsvet-100 chromatograph with a flame-ionization detector and a glass column (adsorbent weight 0.3 g, nitrogen as carrier gas). Samples of test sorbates were introduced as a vapor—air mixture.

Chromatographic data were processed using a MultiChrom v.152m program (Ampersand Ltd). Retention times were measured, and specific retention volumes were calculated from the latter at different temperatures. Heats of adsorption (Q)[14] were calculated from the temperature dependence of the retention volume. The error of determination of the retention times of the adsorbates was ±0.3%, and that for the heats of adsorption was ±1 kJ mol^{-1}.

The temperature of adsorption measurements did not exceed 100 °C, which is much lower than the temperature interval of catalytic allylbenzene isomerization (>170 °C) and CCl_4 addition to the multiple bond of olefin (>130 °C).

Results and Discussion

The heats of adsorption determined by chromatography for the chosen test sorbates on the catalysts and pure support are presented in Table 1 along with the data on particle sizes and their activity in model reactions (1) and (2).

Table 1. Heats of adsorption of the sorbates (Q), the average diameter of metallic particles (d), and their catalytic activity in model reactions

Parameter	γ-Al_2O_3	M/γ-Al_2O_3				
		Ni (0.3%)[a]	Au (0.4%)[b]	Au (0.55%)[a]	Au (5%)[b]	Au (0.4%) + Ni (0.3%)[a]
Adsorbate			Q/kJ mol^{-1}			
n-C_6H_{14}	27	27	51	53	39	61
n-C_7H_{16}	32	31	55	57	42	64
n-C_8H_{18}	37	34	60	61	45	66
CCl_4	45	49	44	46	48	47
$CHCl_3$	48	46	49	49	49	50
C_6H_6	30	28	27	28	27	35
C_6H_5Me	49	48	49	48	47	50
C_6H_5All	51	50	71	68	55	79
Oct-1-ene	39	42	75	68	66	90
Isooctane	26	26	43	40	23	52
Particle			d/nm			
	—	50	3	3	23	3, 60 [c]
Reaction		Activity/(mole of product) (mole of Au)$^{-1}$ h^{-1}				
Isomerization of C_6H_5All	0	0	20	20	3	3100
Addition to oct-1-ene	0	0	20	17	4	30
Addition to C_6H_5All	0	0	14	13	2	85

[a] Prepared by the metal vapor synthesis.

[b] Prepared by the anionic adsorption method.

[c] Bimodal distribution.

$$\mathrm{PhCH_2CH{=}CH_2} \xrightarrow[170\ ^\circ\mathrm{C}]{\mathrm{M}_n/\gamma\text{-}\mathrm{Al_2O_3}} \mathrm{PhCH{=}CHMe} \qquad (1)$$

$$\mathrm{RCH_2CH{=}CH_2} + \mathrm{CCl_4} \xrightarrow[130\ ^\circ\mathrm{C}]{\mathrm{M}_n/\gamma\text{-}\mathrm{Al_2O_3}} \mathrm{RCH_2CHClCH_2CCl_3} \qquad (2)$$

M = Au, Ni, Au + Ni; R = Ph, n-C_5H_{11}

Gold nanoparticles supported in approximately equal amounts by the methods of anionic adsorption and metal vapor synthesis possess similar adsorption properties. For instance, the heats of adsorption on the catalysts, which were obtained by anionic adsorption (0.4 wt.% Au) and metal vapor synthesis (0.55 wt.% Au), are virtually the same.

The heats of adsorption of alkanes on pure alumina are somewhat lower than the published values.[15,16] For example, $Q(n\text{-}C_7H_{16})$ on γ-Al_2O_3 is 32 kJ mol^{-1} (see Table 1). The heats of adsorption of n-heptane on γ-Al_2O_3 calculated from published data using extrapolation by the additive scheme[17] are 43.1 [15] and 46.4 kJ mol^{-1}.[16]

The data on adsorption of substances of other classes agree with the known adsorption properties of γ-Al_2O_3. An increase in the basicity of the molecules upon the introduction of alkyl or alkenyl substituents into the aromatic ring determines a stronger adsorption of toluene and allylbenzene as compared with unsubstituted benzene. The lower (compared to that of octane) heat of adsorption is caused by steric hindrance created by alkyl substituents, which decrease the number of effective contacts of the methylene groups of alkane with active adsorption sites of the surface.[18,19]

Gold immobilization exerts no effect on the heats of adsorption of chlorohydrocarbons, benzene, and toluene but increases the heats for sorbates with long alkyl or alkenyl groups, *viz.*, alkanes, olefins, and isooctane (see Table 1). Thus, the increase in the heat of adsorption (ΔQ), when small gold nanoparticles (average diameter 3 nm) appear on the support surface, is equal to 24, 23, and 23 kJ mol^{-1} for hexane, heptane, and octane, respectively. For oct-1-ene containing both the methylene chain and double bond, ΔQ = 36 kJ mol^{-1}. The effect ΔQ of alkanes is low for the samples with relatively large gold crystallites (average diameter 23 nm). The probable explanation of different adsorptions of alkanes on the nanoparticles of different size is that the strong interaction between the metal and hydrocarbons occurs only with special, coordinatively unsaturated metallic sites (vertices, edges, cracks, and other "roughness").[20] Undoubtedly, the smaller is the size of the nanocluster, the higher is the fraction of such strongly nonequilibrated areas on the nanocluster surface .

The increase in the heat of adsorption of alkanes and olefins on the Au + Ni/γ-Al_2O_3 sample is higher than that on the monometallic systems. As can be seen from the data in Table 1, for the immobilization of comparatively large nickel nanoparticles (50 nm), the heats of adsorption of all the substances under study coincide within the experimental error with those obtained for the pure support. Thus, the nickel itself does not compete with the support for sites of hydrocarbon adsorption. However, being added into the composition of the mixed particles (Au + Ni), nickel favors, most likely, the formation of additional defects, which activate gold atoms. A possibility of similar activation is indicated by literature data[21] on the bimetallic nanoparticles.

Let us attempt to compare the strength of adsorption with the catalytic activity of the M/γ-Al_2O_3 samples in transformations of the corresponding unsaturated substrates.

The heat of adsorption of allylbenzene on γ-Al_2O_3, which is catalytically inactive in reactions (1) and (2), equals 51 kJ mol^{-1}. The same values within the measurement error were obtained for Ni/γ-Al_2O_3, which is also catalytically inactive in these reactions. The increase in the heat of adsorption of allylbenzene on all mono- and bimetallic gold-containing systems above 51 kJ mol^{-1}, induces a measurable catalytic activity of these samples in reactions (1) and (2). This activity changes in parallel to the heat (see Table 1). A similar change in the catalytic activity of M/γ-Al_2O_3 (M = Au, Au + Ni) in the addition of CCl_4 to the multiple bond of C_8H_{16} at different heats of olefin adsorption is also observed for oct-1-ene.

Thus, the heats of adsorption can serve as indicators of the activity of the gold-containing systems in the processes including the step of activation of unsaturated compounds by the interaction with the metal.

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References

1. *Nanotechnology Research Directions: IWGN Workshop Report*, Ed. M. Roco, Reidel, Dordrecht, 2000.
2. C. Milone, M. L. Tropeano, G. Gulino, G. Neri, R. Ingoglia, and S. Galvagno, *Chem. Commun.*, 2002, 869.
3. A. Sárkány, A. Horvath, and A. Beck, *Appl. Catal. A: Gen.*, 2002, **229**, 121.
4. J. E. Bailie, H. A. Abdullah, J. A. Anderson, C. H. Rochester, N. V. Richardson, N. Hodge, J. G. Zhang, A. Burrows, C. J. Kiely, and G. J. Hutchings, *J. Phys. Chem. Chem. Phys.*, 2001, **3**, 4113.
5. C. Mohr and P. Claus, *Sci. Progr.*, 2001, **84**, 311.
6. C. Qi, T. Akita, M. Okumura, and M. Haruta, *Appl. Catal. A: Gen.*, 2001, **218**, 81.

7. H. Ito, T. Yajima, J. Tateiwa, and A. Hosomi, *Chem. Commun.*, 2000, 981.
8. A. Malinowski, W. Juszczyk, J. Pielaszek, M. Bonarowska, M. Wojciechowska, and Z. Karpin´ski, *Chem. Commun.*, 1999, 685.
9. H. Sakurai, A. Ueda, T. Kobayashi, and M. Haruta, *Chem. Commun.*, 1997, 271.
10. H. Sakurai and M. Haruta, *Appl. Catal. A: Gen.*, 1995, **127**, 93.
11. A. Ueda and M. Haruta, *Gold Bull.*, 1999, **32**, 3.
12. S. A. Nikolaev, A. Yu. Vasil´kov, V. V. Smirnov, and L. A. Tyurina, *Kinet. Katal.*, 2005, **46**, 915 [*Kinet. Catal.*, 2005, **46** (Engl. Transl.)].
13. S. A. Nikolaev, V. V. Smirnov, S. N. Lanin, and L. A. Tyurina, *Tez. dokl. XXIII Vseros. simp. molodykh uchenykh po khimicheskoi kinetike* [*Proc. XXIII All-Russia Symposium of Russian Young Scientists on Chemical Kinetics*] *(Klyaz´ma, Moscow Region, March 14—17, 2005)*, Moscow, 2005, 54 (in Russian).
14. A. V. Kiselev, D. P. Poshkus, and Ya. I. Yashin, *Molekulyarnye osnovy adsorbtsionnoi khromatografii* [*Molecular Foundations for Adsorption Chromatography*], Khimiya, Moscow, 1986, 272 pp. (in Russian).
15. S. A. Greene and H. Pust, *J. Phys. Chem.*, 1958, **62**, 55.
16. E. Koberstein, *Z. Elektrochem.*, 1960, **64**, 906.
17. A. A. Kubasov, I. V. Smirnova, and K. V. Topchieva, *Kinet. Katal.*, 1964, **5**, 520 [*Kinet. Catal.*, 1964, **5** (Engl. Transl.)].
18. A. V. Kiselev and Ya. I. Yashin, *Zh. Fiz. Khim.*, 1966, **40**, 603 [*Russ. J. Phys. Chem.*, 1966, **40** (Engl. Transl.)].
19. E. V. Kalashnikova, A. V. Kiselev, R. S. Petrova, and K. D. Scherbakova, *Chromatographia*, 1971, **4**, 495.
20. B. Coq and F. Figueras, *Coord. Chem. Rev.*, 1998, **178—180**, 1753.
21. A. Y. Stakheev and L. M. Kustov, *Appl. Catal. A: Gen.*, 1999, **188**, 17.

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