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Structure of catalytically active gold nanoparticles by XAFS spectroscopy

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Abstract. A series of Au/Al₂O₃ catalysts prepared by the different procedures and series of model system Au/Si(100), Au/Si(111) differing in the mean Au particle sizes (from 2 nm up to 30 nm) were studied by EXAFS and XANES techniques. No visible changes in electron states of Au for all samples prepared by different methods in comparison with bulk material were detected. Oxygen atoms were not detected around Au atoms within the detection limits of our study (a few per cents of surrounding atoms). A gradual reduction of the Au-Au bond length and first shell Au-Au coordination number and an increase in the Debye-Waller factor are observed as the size of supported Au particles decreases. The significant increase of structural disorder for the smallest Au particles comparatively to the bulk Au metal and sizeable particles was detected. These variations in micro-structural parameters of Au nanoparticles are in line with an increase in their catalytic activity in CO oxidation. For model systems some coordination of Au- atoms from islands and Si- atoms from crystal surface was detected for thin Au "films".

1. Introduction

The catalytic activity of the nanosized gold particles (in contrast to the bulk gold materials) is well established at present. The extraordinary activity of gold particles has been shown for the various catalytic processes such as CO oxidation, including selective oxidation in the presence of hydrogen for fuel cell application [1, 2]. While the number of discovered reactions catalyzed by nanosized gold is constantly increasing, the origin of the superior catalytic activity of gold nanoparticles has not been well understood. There is a lack of systematic studies combining physical and chemical methods of research of the influence of particle size on electronic, structural and catalytic properties of the supported gold. One of the main problems in this direction is the limitations of physical methods applied to the study. For example, the X-ray diffraction is not visible for small metal particles (< 5 nm), the transmission electron microscopy is not sensitive to ionic gold, etc.

It has been shown earlier by the X-Ray spectroscopy methods that spectra of occupied and vacant electron states of supported Ni nanoclusters in catalysts change their parameters as the size of supported Ni particles decreases down to 1,5 - 2 nm [3, 4]. The application of synchrotron-based X-

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Ray spectroscopy methods such as XANES and EXAFS can shed more light on physical, electronic properties and peculiarities of microstructure of the Au-catalysts. Both methods are not restricted to the materials with long range order, and by now, there are already some results obtained in this direction [5-11]. At the same time, these results contain contradictions and raise many questions, more particularly concerning interatomic distances and valence states changes for small Au particles. Our XAFS measurements for supported Au nanoparticles at lower temperature provide more precise and reliable results and study the Debye-Waller factor temperature dependences. In our previous paper [11] we employed samples with various sizes of Au- particles on Al₂O₃ prepared by deposition precipitation (DP) method only. Goal of this paper is an XAFS- comparative investigation of microstructure, electronic and chemical properties alteration for the alumina-based Au- catalysts and model systems containing Au on Si- single crystal depending on particles sizes and method of preparation too. Identification of possibly different electronic states in gold particles and their comparison with catalytic properties of these samples helps to identify electronic states of the supported gold which are more active for the catalytic reactions chosen.

2. Experimental

EXAFS and XANES spectra of the Au L_{III} absorption edge were measured at the DUBBLE beamline (BM26A) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) at 12 and 296 K and at the VEPP-3 storage ring of the Budker Institute of Nuclear Physics (Novosibirsk, Russia) at room temperature only. The X-ray absorption measurements were carried out with both the conventional procedure, by direct measurements of X-ray absorption coefficient for the Au/Al₂O₃ catalysts, and by using the X-ray fluorescence mode for the series of model system Au/Si(100) and Au/Si(111). Contemporary experimental setup of the DUBBLE beamline described in [12] at length. Preparation of the samples of model and real catalysts, as well as catalytic testing, was carried out at the Boreskov Institute of Catalysis (Novosibirsk). Samples have been tested in CO oxidation, the mean Au particle sizes values were determined from TEM (transition electron microscopy) micrographs. Systems with gold particles for the model samples were prepared by the deposition of metallic gold in UHV on Si- single crystals. Effective thickness of Au "films" was controlled by synchronous measurement of Au4*f* electron spectra intensity. The variation of Au "films" effective thickness, or gold particle size, was achieved both by variation of deposition time and by sintering the prepared gold particles at various temperatures.

Real catalysts preparation methods included: 1) deposition precipitation (DP) – samples 1, 2, 4, 6, 7, 9 prepared by adsorption of anionic Au(III) hydroxide complexes and calcined in air at 400°C, sample 6 is sample 7 treated by water vapor at 700° C; 2) chemical vapor deposition (CVD) – sample 3 (treated in air at 220° C); 3) adsorption of $(CH_3)_2Au(acac)$ (CLPG) – sample 8 (treated in air at 400° C); 4) impregnation by aqua solution HAuCl₄ (IMP) - sample 10 (treated in H₂ at 400° C), sample 5 is sample 10 washed by solution [(CH₃)₄]NOH.

3. Results and discussion

The Au L_{III} XANES spectra for the Au/Al₂O₃ samples (see table 1) were compared with the spectrum from Au foil. In spite of variation in the mean Au particle diameter value from ~2 to ~30 nm, the Au L_{III} XANES spectra of all the supported Au catalysts studied are very close to each other and to the spectrum of bulk Au metal in their shape and the feature positions. This result is the same as in our previous study [11]. To observe the tiny changes in the spectra, if any, first derivatives of the XANES spectra were calculated. Again, the shape and positions of all features for the supported Au particles match those of the bulk gold metal. Thus the data indicate no visible changes in electron states of Au and the absence of familiar three-valence gold of usual gold oxide species (characterized in Au L_{III} XANES spectra by "white line" over absorption edge) at least within the detection limits of our experiments (more or equal a few per cents of Au atoms) in the samples under investigation.

Figure 1 shows experimental $k^2\chi(k)$ Au L_{III} EXAFS spectra (k^2 -weighted) of the Au/Al₂O₃ catalysts and Au foil (samples 1-10 and 11, table 1) measured at 12 K. The curves are presented in order of decreasing the mean Au particle size in the sample (from top to bottom). Table 1 shows characteristics

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of dispersed catalysts samples and EXAFS fit parameters for the samples 1–10 and Au foil at 12 and 296 K.



Figure 1. Experimental $k^2 \chi(k)$ Au L_{III} EXAFS spectra (k^2 -weighted) of the Au/Al₂O₃ catalysts (see table 1) and Au foil measured at 12 K.

In good accordance with the literature data, the Au-1, 2, 4 samples with smaller Au particle sizes (< 5 nm) demonstrated the high catalytic activity in CO oxidation at 313 K, whereas the Au-8, 9, 10 samples containing exclusively the Au particles of more than 5 nm in size were catalytically less active (table 1). Au- nanoparticles size distribution calculated from TEM shows that samples 6 and 7 characterized by simile mean sizes, obviously, differ in the presence of dispersive Au that

are responsible for activity in CO oxidation. So, it can be safely suggested that sample 6 in contrast to sample 7 has a smaller proportion of catalytic active Au particles of less than 5 nm in size. The coordination number for the first Au shell (N), interatomic Au-Au distance (R) and Debye-Waller factor (S^2) found for the Au 6 - 10 sample are also similar to those of the bulk metal (see table 1). This result is rather expected, since the sizes of Au particles contained in these samples ($d_i = 10-15$ nm) are large enough for these particles to contain a very small portion of near-surface Au atoms and may exhibit the metallic properties. From the Au-5 sample to the Au-1 sample a monotonic decrease of the Fourier transform magnitude |F(R)| for five coordination shells is observed with decreasing mean Au particle size. Since the magnitude as a first approximation is proportional to Au-Au coordination number, our observation means that decreasing N_I value is in line with a reduction in the mean Au particle size. At the same time, the interatomic Au–Au distance decreases and Debye-Waller factor raises two-three times from Au-5 to Au-1 samples.

Table 1. Characteristics of dispersed catalysts samples and EXAFS fit parameters computed from the Au L_{III} $k^2\chi(k)$ data ($\Delta k = 3-18$ Å⁻¹, $S_0^2 = 0,8$) measured at 296 K and 12 K for the Au/Al₂O₃ samples with different mean Au particles sizes (*N* is the first shell Au-Au coordination number, *R* is the Au-Au bond length, σ^2 is the Debye-Waller factor); the catalytic activity in the process of CO oxidation was estimated by the arbitrary fivefold scale.

Ма	Preparation	[Au],	TEM	Catal.	Ν	<i>R</i> , (Å)	<i>R</i> , (Å)	$2\sigma^2$, (Å ²)	$2\sigma^2$, (Å ²)
JN⊡	method	weight %	Size, nm	activ.	12 K	296 K	12 K	296 K x10 ⁻²	12 K x10 ⁻²
1	DP	1,6	2,3	4	8,18	2,830	2,846	1,67	0,73
2	DP	1,5	2,8	5	10,23	2,831	2,859	1,75	0,56
3	CVD	1,0	2,5-3,0	2	9,87	2,839	2,860	1,71	0,39
4	DP	1,8	4,0	4	10,6	2,842	2,864	1,64	0,43
5	IMP	2,3	4,2	3	11,6	2,848	2,869	1,58	0,37
6	DP	1,7	9,8	5	11,57	2,849	2,868	1,57	0,33
7	DP	1,7	11,0	3	11,31	2,850	2,868	1,59	0,29
8	CLPG	3,8	13,3	0	12,2	2,854	2,870	1,50	0,30
9	DP	1,6	16,5	1	12,05	2,855	2,871	1,50	0,27
10	IMP	2,4	4,1	0	12,37	2,855	2,872	1,47	0,28
11	Au foil				12	2,857	2,872	1,49	0,26

The decrease of the interatomic Au-Au distances accompanying the decrease in Au particles size is qualitatively in agreement with the earlier published data. However, quantitatively, these results do not match with the data from [8-10]. The possible reasons of this contradiction were discussed in [11]. Including oxygen or Al atoms in the first coordination sphere of Au did not improve the fitting. To be specific, oxygen atoms were not detected around Au atoms within the detection limits of our study (a few per cents of surrounding atoms).

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Comparative analysis in harmonic approximation of the EXAFS spectra measured at low (12 K) and ambient (296 K) temperatures allows us to distinguish between the contribution of structural and thermal disorders in the bulk metal and supported Au particles. As one can see from Table 1, the Debye-Waller factor for the most dispersed Au-1 catalyst measured at 12 K is about three times higher than that for the bulk gold, while this variation is only 10% at 296 K. This means that the temperature dependence of the Debye-Waller factor for the small Au particles is different from that for the Au foil. At the same time, contraction in the Au-Au bond length measured for the Au-1 catalyst with the highest dispersion as compared with the bulk Au metal remains the same within the accuracy limit both at 12 and 296 K ($\Delta R_1 \approx 0.026-0.027$ Å, Table 1). These results allow the conclusion that significant changes in the interatomic interaction and the increase of structural disorder for the smallest Au particles comparatively to the bulk Au metal and sizeable particles take place. Mention may be made of using inharmonic approximation to fit the EXAFS spectra for samples with small metal particles in [8-10]. In our opinion, addition of inharmonic cumulants for the fitting procedure is non-essential at least at lower temperature (12 K).

Table 2 shows EXAFS fit parameters for the Au/Si(111) and Au/Si(100) samples with different effective thickness of Au films. It was possible to obtain good values of fit index (F_{EXAFS}) for the samples with small effective thickness of deposited Au films taking into account not only Au- atoms but Si- atoms and, in some cases, O - atoms in the first coordination sphere of Au. Thus some coordination of Au atoms from three- dimensional islands and Si- crystal surface was detected for model system with thin Au "films".

Table 2. EXAFS fit parameters computed from the Au $L_{III} k^2 \chi(k)$ data ($\Delta k=3-12 \text{ Å}^{-1}, S_0^2=0.8$) measured at 296K.
for Au/Si(111)- and Au/Si(100)- samples with different effective thickness (in Å or number of monolayers
(MLs)) of deposited Au films (islands) (NAU, NSI, NO are the first shell Au-Au, Au-Si, Au-O coordination
numbers, R_{Au-Au} is the Au-Au bond length, σ^2_{Au-Au} is the Au-Au Debye-Waller factor, E_0 is the energy threshold,
F_{EXAFS} is the goodness of fit index).

Sample	Effective thickness of Au films	N _{Au}	N _{Si}	No	R _{Au-Au} , (Å)	$-E_0,$ (eV)	$2 \sigma^{2}_{Au-Au^{*}} 10^{3},$ (Å ²)	F _{EXAFS}
A(111)	~1000 Å	12			2,875	-7,65	17,8	0,9
A(100)	~1000 Å	12			2,872	-8,17	21,4	1,0
B(111)	~2,5ML	9,6±0,5	$0,4\pm0,1$	-	2,847	-6,58	21,2	1,2
B(100)	~2,5 ML	10,9±0,4	-	-	2,844	-6,76	22,8	1.0
C(111)	~1,3 ML	$8,8{\pm}0,4$	$0,5\pm0,1$	-	2,838	-6,82	21,8	0,3
C(100)	~1,3 ML	9,5±0,5	$0,6\pm0,1$	-	2.853	-6,92	20,7	1,2
D(100)	~0,8 ML	$7,9\pm0,2$	$0,5\pm0,1$	$0,6\pm0,1$	2,838	-5,30	19,7	1,0
E(111)	~0,4 ML	8,2±0,2	$0,4{\pm}0,1$	$0,4{\pm}0,1$	2,833	-6,63	26,4	0,4

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5. References

- [1] Haruta M 1997 Catal. Today. 36 153
- [2] B.L. Moroz, P.A. Pyrjaev, V.I. Zaikovskii, V.I. Bukhtiyarov 2008 Catal. Today. 144 292
- [3] Erenburg S B, Golovin A V, Noskova S P et al 1974 React. Kinetics and Catalysis Letters 1 507
- [4] Ovsyannikova I A, Erenburg S B et al 1976 Izvestiya AN SSSR. Ser. fiz. (in Russian) 40 230
- [5] Guzman Javier and Gate Bruce C 2002 J. Phys. Chem. B 106 7659
- [6] Chen M S and Goodman D W 2006 Catalysis Today 111 22
- [7] Radnik J, Wilde L, Schneider M et al 2006 J. Phys. Chem. B 110 23688
- [8] Van Bokhoven J A, Louis C, Miller J T et al 2006 Angewandte Chemie (Int. Ed.) 45 4651
- [9] Weiher N, Bus E, Delannoy L et al 2006 *Journal of Catalysis* 240 100
- [10] Miller J T, Kropf A J, Zha Y et al 2006 Journal of Catalysis 240 222
- [11] Erenburg S B, Moroz B L, Bausk N V et al 2007 Nucl. Inst. @ Meth. Phys. Res. A 575 105
- [12] Sergey Nikitenko, A.M.Beale, Ad M. J. van der Eerden et al 2008 J. Synchrotron Rad. 15 632