

Report on the beam time for the project 26 01 753
(DUBBLE station BM26A at the ESRF)
“XANES and EXAFS study of electronic and structural properties of nanosized gold particles on alumina and iron oxide”

Very high activity of supported catalysts containing gold nanoparticles in CO oxidation reactions at low temperatures has been described first in [1]. A large number of studies concerning such kind of materials have been reviewed in many papers, for example [2, 3, 4]. It has been shown by many authors that the activity increases when Au particle size decreases especially in the region less than about 50Å. Any data concerning the particles size and its distribution compared with the catalysts activity can be used as a base for catalytic reaction models construction materials and nanoparticles [5]. Recently nanoscale gold particles have been studied successfully in supported catalysts using EXAFS and XANES spectroscopy [6,7].

EXAFS and XANES spectra at the AuL_{III} absorption edge have been measured at 296 K and 12 K. Si(111) single crystal operating at sagittal focusing mode has been used as a monochromator. Au/Al₂O₃ samples have been prepared by DP (deposition-precipitation), CVD (chemical vapor deposition) and LPG (Liquid Phase Grafting). Evaluated catalytic activity in CO oxidation reaction in arbitrary 5 units scale can be used to compare the samples.

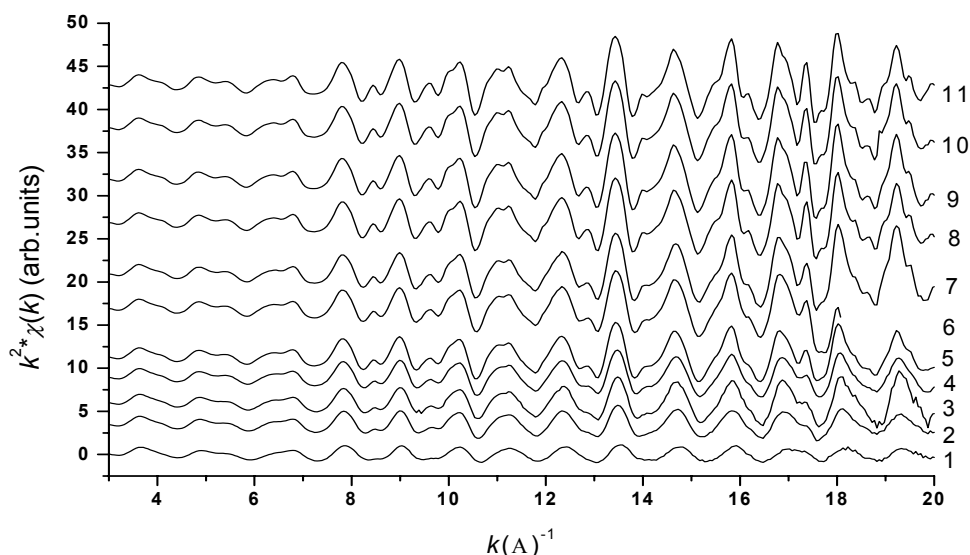


Figure 1

Figure 1. AuL_{III} EXAFS spectra measured at 12 K.

Normalized oscillating part of X-ray absorption $\chi(k)$, demonstrate very low noise level even in high k region at 12 K temperature as well as at 296 K. Samples are arranged in the Figure 1 from number 1 to 10 according to EXAFS data amplitude increase for 5 Au coordination shells which is proportional to coordination numbers and particle size, respectively [8]. Au foil has been used as a reference sample and is marked by number 11 in the Figure 1.

Fourier transform magnitudes for all the spectra measured at 296 K and 12 K clearly exhibit Au-Au peaks only, corresponding to metal foil, up to fifth shell. No any bonds of Au atoms with light atoms have been found. Peaks, corresponding to the first Au-Au shell have been filtered in the region 1.6Å -3.2 Å for all spectra measured. Fourier filtered $k^2\chi(k)$ have been fitted 3Å⁻¹-16Å⁻¹ region using EXCURV-98 package included in DLV package. S₀ parameter has been fixed in all cases to 0.8.

All the XANES spectra presented in the Figure 1 exhibit all the bulk metals peculiarities only without visible admixture of any other phase. As has been mentioned above $|F(R)|$ curves for all spectra reproduce bulk metal peaks with varying amplitudes. These facts give clear evidences that samples under the study contain metal particles only with varying size. Samples 8, 9, 10

demonstrate on the $|F(R)|$ curves close amplitudes to the bulk metal as well as very close coordination numbers, interatomic distances and Debye-Waller factors as the fitting result. It means that these three samples contain big clusters in which part of near-surface atoms is small. Samples 7-1 demonstrate monotonic peaks amplitude lowering on the $|F(R)|$ curves for 5 coordination shells. In parallel for this raw Debye-Waller factor rising, interatomic distance decreasing ($\Delta = 0.01\text{--}0.03$ Å) and coordination number lowering from 12 to 8 can be seen. Catalytic activity and Au particles dispersion rise in this row with some exceptions.

Our result concerning interatomic distances obtained from fitting procedure decrease in parallel with the dispersion increase is in consistence with [6, 7] data. At the same time distances decrease in our case much more small. This difference can be explained by the fact that in [6, 7] Au particles containing only several atoms has been studied. Moreover our EXAFS measurements were realized at lower temperature (12 K) and unharmonic cumulants calculation, increasing real interatomic distances [9] is inessential in our case in contrast with measurements in [6,7]. Furthermore in our case E_0 parameter, anticorrelating with R parameter in the fitting procedure, shows less changes from sample to sample confirming results reliability.

As far as EXAFS spectra have been measured at 12 K and 296 K one can try to separate structural and thermal disorder in the bulk metal and nanoclusters. It was determined for the most active samples with the smallest clusters the Debye-Waller factor at 12 K almost three times higher than for bulk metal, while at 296 K only 10% higher. The same time interatomic distance difference between these samples and the bulk metal remains the same within the accuracy limits at two temperatures. It means that for the bulk metal and small Au particles the Debye-Waller factor temperature dependence is different. Supposing the harmonic approximation validity one can conclude the structural disorder and interatomic interaction strength difference in these samples as well as respective potential changes.

At the same time, some authors try to use unharmonic approximation for small metal particles and add the third and fourth cumulants to the phase and amplitude of the EXAFS function, correspondingly [9]. However, unharmonic cumulants addition, apparently, is inessential in our case for EXAFS measurements at lower temperature (12 K).

Using results obtained in [8] and coordination number for the first shell for the sample 1 we can estimate a number of Au atoms in its nanoclusters as about 100 ± 20 atoms. More accurate results coordination numbers for the second and third shells will be determined and can be used for nanoparticles sharp determination follow [8].

Gradual decrease of interatomic distances, coordination numbers as well as increase of Debye-Waller factors has been found for the first shell of Au atoms in nanoparticles for the sample raw in parallel with CO oxidation catalytic activity rising. Valuable changes of structural disorder and interatomic interaction strength for smallest nanoclusters and bulk metal have been supposed applying the harmonic approximation model. Sizes of the smallest Au clusters have been evaluated using coordination number variation for the first shell.

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[1] M. Haruta, T. Kobayashi, H. Sano and N. Yamada, Chem. Lett. 2 (1987) 405

[2] M. Haruta, J. New Mater. Electrochem. Syst. 7 (2004) 163

[3] R. Meyer, C. Lemire, S.K. Shaikhutdinov and H.-J. Freund, Gold Bulletin 27 (2004) 72

[4] G.J. Hutchings, Catal. Today 100 (2005) 55

[5] D.C. Koningsberger and R. Prins. X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES 1988 New York, Wiley 710

[6] N. Weiher, E. Bus, L. Delannoy, C. Louis, D.E. Ramaker, J.T. Miller and J.A. van Bokhoven, J. of Catal. 240 (2006) 100

[7] J.T. Miller, A.J. Kropf, Y. Zha, J.R. Regalbutto, L. Delannoy, C. Louis, E. Bus and J.A. van Bokhoven, J. of Catal. 240 (2006) 222

[8] A. Jentys, Phys. Chem. Chem. Phys 1 (1999) 4059

[9] Eveline Bus, Jeffrey T. Miller, A. Jeremy Kropf, Roel Prins and Jeroen A. van Bokhoven, Phys. Chem. Chem. Phys. 8 (2006) 3248