Electronic and Geometric Structures of Small Gold Metal Particles: Particles Size Effects and the Relationship to Catalytic Activity

Jeroen A. van Bokhoven[1,*], Jeffrey T. Miller[2]

[1]*Institute for chemical and Bioengineering, ETH Zurich, Switzerland; j.a.vanbokhoven@chem.ethz.ch*
[2]*BP Research Center, Naperville, IL 60565-8406 USA*

Abstract. The structure of supported gold nano-particles is affected by the size of the particles. Smaller metal particles have decreased gold - gold bond lengths, a higher d electron count, and have a more reactive d band. The influence of support is negligible compared to that of particle size.

Keywords: Gold catalysis; Charge-transfer; XANES; Whiteline; Particle size effect; Support effect; Bond length; d electrons
PACS: 85.45.Jn

INTRODUCTION

Metal nano-particles supported on oxides and carbon carriers are used as catalyst in many large-scale industrial processes. Activity and selectivity strongly depend on particle size and type of support. The origins of these differences are poorly understood. Bulk gold is completely inert towards reaction with molecules, however, when finely dispersed, gold catalysts show high activity and selectivity in oxidation and hydrogenation reactions. The particle size is an important factor in determining activity of these nano-particles. Particles smaller than five nm, and especially below about 3 nm, show high activity [1]. Other metals also show particle-size dependence in activity and selectivity.

X-ray absorption spectroscopy (XAS) is an important tool in studying structure - performance relations in catalysis, because the local atomic structure can be determined under in situ conditions. In case of L-edges, both electronic and geometric structures can be determined. The L_3 edge shows a whiteline, which reflects the number of holes in the d band. A more intense whiteline correlates to more holes in the d band and higher oxidation states. Over the years we have synthesized gold catalysts of varying size on various oxide supports. This series enabled us to determine the relationship between particle size and number of d electrons and do this on various supports. Using FEFF8, the experimental spectra were simulated and the structure of the d band was calculated. Implications of these findings for catalytic activity are discussed.

EXPERIMENTAL

L_3 edge XAS spectra were measured on the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. A cryogenically cooled double-crystal Si (111) monochromator and an uncoated glass mirror to reduce the higher harmonics were employed. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.07 sec per data point. Measurements were made in transmission. A gold foil spectrum was acquired simultaneously with each measurement for energy calibration.

Supported gold catalysts on Al_2O_3, SiO_2, TiO_2, ZrO_2, CeO_2, and Nb_2O_5 were prepared by deposition precipitation using $HAuCl_4$. The pH of the solution depended on the isoelectric point of the support and chlorine was removed using a base [2]. Precursor catalysts were activated in hydrogen at 175 to 250°C for 1 hour in of 4% H_2/He prior to measurement. Full multiple scattering calculations were performed using the FEFF8 code [3]. The bulk structure of gold was assumed and the cluster size was between 13 and 55 atoms. The DOS of the center atom in the clusters is presented.

RESULTS

Particle sizes of all catalysts after reduction were determined from full EXAFS analyses via the coordination number [2]. Figure 1 shows the shortening of the gold - gold bond length with decreasing particle size. The maximum decrease in bond length is 5.5%. Bond length contractions in small gold particles have been observed before and also in various other metals using EXAFS and via determination of the lattice spacing in X-ray or electron diffraction [4].

Although different supports have different surfaces exposed, which may affect the structure of the gold particles, there is no clear support effect on the bond length. The bond length is dominated by particle size.

The whiteline in L_3 edges is representative of the number of holes in the d band. The L_3 edge of bulk gold shows a small whiteline, because hybridization of

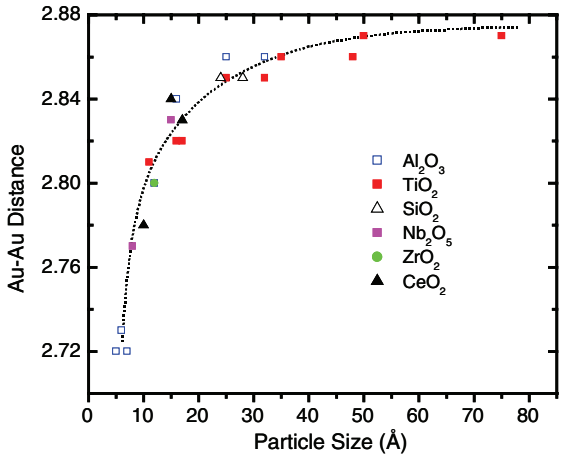

FIGURE 1. Gold - gold bond length as function of coordination number over supported gold catalysts. Data from [2] are used to produce the plot.

the s, p, d orbitals causes charge-rearrangement between the s, p, and d orbitals. The electron occupation in bulk gold is $6sp^{1+x}5d^{10-x}$ [5]. For all catalysts the difference in their whiteline intensity with that of bulk gold was determined and plotted in Figure 2 as function of particle size. Smaller particles have smaller whitelines than bulk and, therefore, a higher number of electrons in the d band. Because fewer atoms contribute to the s, p, and d bands, the bands are narrower, and overlap less. Consequently, small particles show less hybridization and therefore less charge-rearrangement. All catalysts in Figure 2 followed the same trend and there was no influence of type of support. Although charge transfer from and to the support has been often suggested, no evidence of an increased or decreased number of electrons in the d band was observed. The dominant factor that determines the electronic structure measured in the whiteline was the particle size. Different supports and synthesis methods do not affect the gold - gold bond length or number of d electrons.

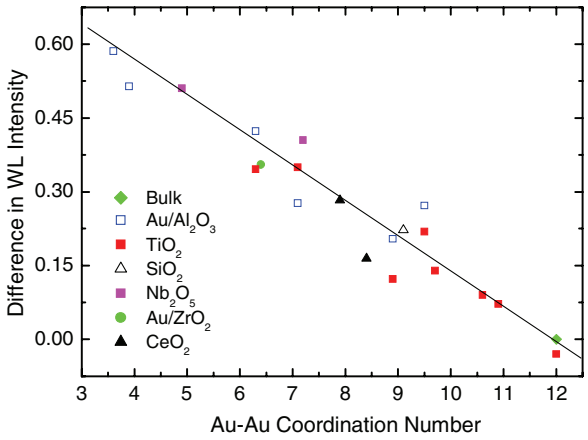

FIGURE 2. Difference in intensity of the whiteline of the spectrum of bulk gold and that of supported nano-particles. Data from [3] were used to produce the plot.

FEFF8 calculations were successfully used to mimic the experimental spectra [3] (not shown) and to calculate the d DOS (Figure 3). Because smaller particles have fewer atoms, the d band is much narrower in these particles. The filling of the band, however, remains close to ten, slightly decreasing with increasing particle size. Consequently, the energy of the d band, taken as its averaged energy, is higher for smaller particles [3].

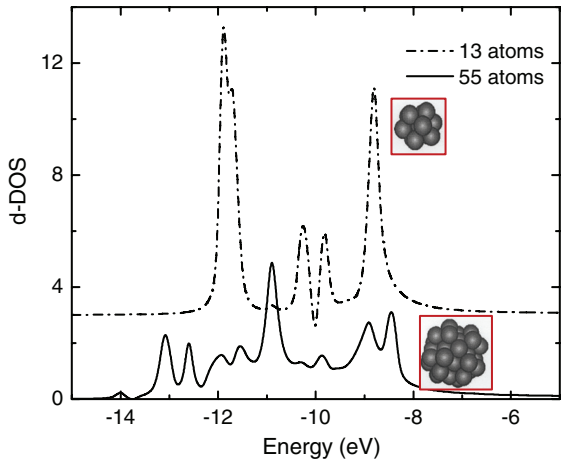

FIGURE 3. FEFF8-calculated d-DOS of gold clusters with various numbers of atoms in the cluster.

DISCUSSION

Although catalytic reactions over gold particles show a very large effect of the support, no systematic changes in the properties of gold nano-particles on different supports were observed. The average gold-gold distance and the number of d electrons change with particle size and no effect of the support is observed. Although, it has been widely assumed that charge-transfer occurs between support and metal nano-particles, there is no evidence in our data for that based on the number of holes in the d band (Figure 2).

The reactivity of d-transition metals depends on the energy of their d band. From left to right in the periodic Table, the d band moves down in energy and, after adsorption of an adsorbate, less antibonding states become depopulated and the metal-adsorbate bond becomes weaker [6]. On the left, very strong adsorption may occur and these metals show little catalytic activity because the surface is poisoned. On the right the surfaces are bare and no reaction can occur on the surface. Bulk gold is therefore inert to corrosion and shows no or very low catalytic activity [1]. However, small nano-particles have a d band whose energy is closer to the Fermi level (Figure 3). This will affect their reactivity and may cause the smaller particles to adsorb reactants. After adsorption, these molecules may react, which could explain the catalytic activity shown by small gold particles [3]. It has been experimentally observed that gold nano-particles interact with hydrogen and oxygen [2,7,8], while single crystals of gold are inert towards these molecules.

CONCLUSIONS

The electronic properties and local structure of gold atoms in small nano-particles supported on oxidic supports are affected by particle size. The number of d electrons in the d band increases with decreasing particle size, irrespective of the support. The gold-gold bond length is contracted in smaller particles. The d band of small gold nano-particles is more reactive than that in larger particles, which may affect their catalytic activity. The particle size effect dominates that of the support.

ACKNOWLEDGMENTS

C. Louis, J. R. Regalbuto, and L. Delannoy are thanked for synthesis of part of the samples; A. J. Kropf, Y. Zha, and E. Bus for their help during the measurements and analysis.

REFERENCES

1. G. C. Bond, D. T. Thompson, *Gold Bull.* **33**, 41 (2000).
2. J. T. Miller, A. J. Kropf, Y. Zha, J. R. Regalbuto, L. Delannoy, C. Louis, E. Bus, J. A van Bokhoven, *J. Catal.* **204**, 222-234 (2006)**.**
3. J. A. van Bokhoven, J. T. Miller, submitted
4. G. H. Via, J. H. Sinfelt, F. W. Lytle, *J. Chem. Phys.* **71** 690-699 (1979); P. Lagarde, T. Murata, G. Vlaic, E. Freund, H. Dexpert, J. P. Bournonville, *J. Catal.* **84,** 333-343 (1983); E. C. Marques, D. R. Sandstrom, F. W. Lytle, R. B. Greegor, *J. Chem. Phys.* **72**, 1027-1034 (1982).
5. L. F. Mattheiss, R. E. Dietz, *Phys. Rev. B* **22**, 1663 (1980); M. G. Mason, *Phys. Rev. B* **27**, 748 (1983).
6. B. Hammer, J. K. Nørskov, *Nature* **376**, 238-240 (1995).
7. E. Bus, J. T. Miller, J. A. van Bokhoven, *J. Phys. Chem. B* **109**, 14581-14587 (2006).
8. J. A. van Bokhoven, C, Louis, J. T. Miller, M. Tromp, O. V. Safonova, P. Glatzel, *Angew. Chem. Int. Ed.* **45** 1–5 (2006).