X-ray absorption spectroscopy on gold catalysts

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Gold catalysts are interesting e.g. in the fields of CO oxidation, selective hydrogenation and selective oxidation of propylene [1,2]. The activity is strongly dependent on the dispersion of gold and on the support [1-4]. The smaller the gold particle size, the higher is the activity, which has led to the conclusion that low-coordinated gold atoms [4] or sites at the interface [1] are important for the reaction. Since X-ray absorption spectroscopy (XAFS) can be used to give information on both the oxidation state and the particle size *in situ*, it is a powerful tool for the analysis of gold catalysts. Moreover, it can be used to guide the development of suitable preparation procedures. In most cases gold catalysts are prepared by deposition of a gold precursor on the support, which is reduced to the metallic state by heating in nitrogen, air, or hydrogen [1]. We will here give some examples on how XAFS can give information *in situ* on the formation of the gold particles and how the gold particle size can be estimated. The experiments were performed at beamline X1 with a setup similar to that described in ref. [5]. The gas composition was on-line monitored by mass spectrometry.

Alumina is an important catalyst support, especially due to its high surface area and low cost. Fig. 1 shows the EXAFS results during decomposition of a gold precursor on this support in 2%H_2/N_2. If the catalyst is reduced at 120 °C for about 1 h, the catalyst is only partly reduced. In the XANES spectrum this is indicated by the presence of a low-intensity whiteline and in the Fourier transformed spectrum (Fig. 1b) some Au-Cl (from the $HAuCl_4$ precursor) or Au-O are still present at r = 1.7 Å. Upon heating to 160 °C, gold is fully reduced. Fitting the Au-Au shell with backscattering amplitudes and phase shifts taken from an Au reference foil an apparent coordination number of 9.6 (Table 1) is obtained. This corresponds to a quite large average particle size (30 - 40 Å).

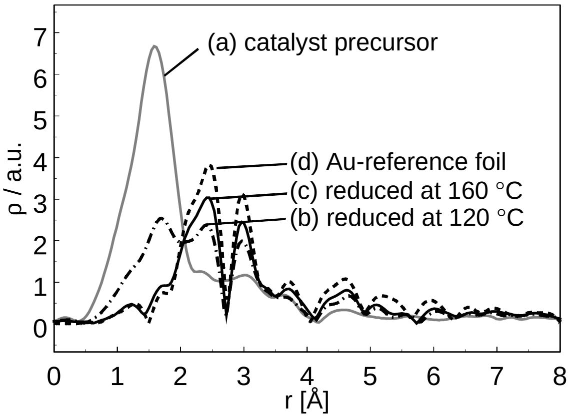

Fig. 1: Fourier transformed EXAFS spectra at the Au,L_3 edge during formation of the gold particles in 2%H_2 in N_2 (3.3 wt% Au on Al_2O_3).

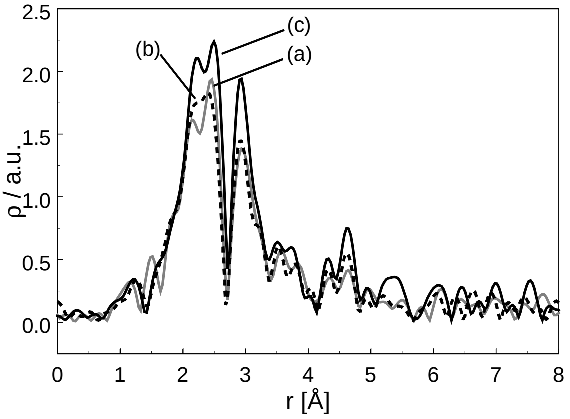

Fig. 2: FT of EXAFS spectra at the Au,L_3 edge in 1%CO/ 21%O_2/inert (1.4 wt% Au on Al_2O_3) after (a) RT; (b) 150 °C; (c) 400 °C.

Smaller particles can be obtained by lowering the loading, by applying another gold precursor or by using gold colloids for the preparation of active gold catalysts [6]. XAFS analysis showed that the use of small gold colloids resulted in Au/Al_2O_3 catalysts with a smaller particle size (Fig. 2a, Table 1). The apparent coordination number (8.3) is significantly smaller than that obtained for the Au/Al_2O_3 catalyst obtained by decomposition of the gold precursor. Also in TEM mainly particles of 20 - 30 Å in size were observed. For more detailed comparison of EXAFS and TEM data, we calculated in a first step the coordination numbers of spherically truncated clusters with different size, listed in Table 2. Clausen and Nørskov [7] recently developed a model, which describes the anharmonic motion of the atoms in the surface regions of such small particles. According to this model the coordination number N^{true} for a fcc metal can be estimated from the apparent coordination number N^{app} using the following relationship

$$N^{true} = N^{app} + f(T)\cdot\alpha\cdot(12 - N^{app}) \qquad (1)$$

where f(T) is a proportionality factor [7] and α the linear expansion coefficient.

Catalyst	**Preparation, activation**	**N^{app} ± 0.5**	**r [Å] ± 0.3**	**σ [Å]**	**N^{true} ± 0.5**	**TEM**
3.3%Au/Al_2O_3	decomp. of gold precursor at 160°C	9.6	2.89	0.09	9.9	40 Å, a few larger
1.4%Au/Al_2O_3	gold colloids, as prepared	8.3	2.89	0.10	8.8	20 – 30 Å
1.4%Au/Al_2O_3	after 150 °C in 1%CO/21%O_2	8.8	2.86	0.10	9.3	-
1.4%Au/Al_2O_3	after 400 °C in 1%CO/21%O_2	9.9	2.91	0.10	10.2	-

Table 1: Apparent coordination numbers, distance, and vibrational amplitudes from the fit of the Au-Au shell of the EXAFS data at the Au,L_3-edge. N^{true} is the coordination number calculated from equation (1).

The true coordination number for the Au/Al_2O_3 catalyst prepared via gold colloids amounts to 8.8 (Table 1), which corresponds to a particle size of 20 - 25 Å (Table 2). This is in good agreement with the TEM results.

Further investigations of the Au/Al_2O_3 catalysts (colloid) in 1%CO/21%O_2/78%Ar showed that they oxidize CO already at room temperature. The particle size hardly changed upon heating to 150 °C (Figs. 2a and 2b, Table 1). However, when the catalyst was heated to 400 °C in the reaction mixture, the particle size significantly increased. This was not observed for e.g. Au/TiO_2 and Au/ZrO_2, probably because a stronger gold-support interaction is present. This facile sintering is probably also the reason that there are not many studies described on Au/Al_2O_3 in literature.

D_{Au-Au} [Å]	Number of Au Atoms	Coord. Number
8.2	19	4.7
12.2	55	6.7
16.3	141	8.1
20.4	249	8.8
24.5	459	9.5
32.6	1061	10.3
40.9	2123	10.7
49.0	3589	11.0

Table 2: Coordination number of spherically truncated clusters.

Comparison of the Au particle sizes from EXAFS and TEM on other Au/MeO_x catalysts revealed that the particle size determination of both methods is in quite good agreement, when the coordination number is calculated according to equation (1). In most cases the average particle size from EXAFS is smaller than that observed in TEM. This simply reflects the different detection limits of the two techniques. TEM cannot detect particles below 10-20 Å whereas XAFS does not have this limitation. Another advantage of XAFS is that the catalysts can be investigated *in situ.* However, comparison with TEM as complementary technique is useful since this technique can give information on the particle size distribution. We have furthermore found that the stability of the small gold particles and their activity were very dependent on the support. Whereas the preparation of small gold particles by decomposition of gold precursors was difficult on Al_2O_3, it is much easier e.g. on the MnO_x support. Work is in progress to apply the fluorescence EXAFS technique in order to get information in cases where the gold loading is very low.

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