Introduction

Since 1980 research has been pursued here on metallic- and bimetallic clusters in which a few metal atoms have been stabilized by CO ligands. After deposition on an inert support such as alumina or Cab-O-Sil these ligands could easily be removed by heat treatment and small supported metal clusters prepared this way. The first paper from our Laboratory on this topic was published in the Proceedings of the 7th ICC held in Tokyo [1].

Later our aim was to find various other methods which lead to narrow size distributions of the supported metal nanoparticles. We proceeded in several directions. Controlled Colloidal Synthesis (CCS) was one of the first techniques we had used for Pd/SiO₂ catalysts [2]. It is a rather simple technique applying silica nanosize particles suspended in an ethanol-toluene binary liquid system of carefully chosen concentration, which provides a high concentration of ethanol in the adsorption layer around the silica nanosize particles and negligible ethanol concentration in the liquid phase. The metal precursor ions diffuse to the thin adsorption layer, where they are reduced by the ethanol and stabilized by the silica support. The second efficient technique was preparation of metal sols, which were adsorbed on to the support [3, 4].

Prof Haruta’s work on gold nano-particles stabilized on various supports stimulated our interest in this research area [5] and our research on nanosized gold catalysts commenced in 1997. Although we started with the deposition-precipitation (DP) method we turned our attention to studying the gold/iron oxide system including two principal aspects: one is a model study of the gold/iron oxide system, and the other, developing novel gold promoted oxide nanolayers.

Investigation on model Au/Fe₂O₃ system

The morphology and electron structure of a Au/FeOₓ/SiO₂/Si(100) catalyst model sample prepared by pulsed laser deposition (PLD) has been investigated by X-ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS), and transmission electron microscopy (TEM) [6].

The valence band of the Au nanoparticles supported on SiO₂/Si(100) measured by UPS is strongly redistributed with decreasing size, involving mostly the lowest and the highest binding energy part of the Au 5d valence states. This effect could be attributed to the redistribution rather than to the narrowing of the 5d states [7-11]. The Au/FeOₓ/SiO₂/Si(100) model system has gold in its zero valence state even during size reduction induced by Ar⁺ ion bombardment. The PLD sample was characterized in the as prepared, oxidized and reduced states, the gold particle sizes being 3.8, 4.1, and 5 nm, respectively. The iron oxide support was amorphous in the as prepared state and after the oxidation, during reductive treatment the amorphous iron oxide was slightly crystallized.
and reduced partly into Fe$^{2+}$ species. Consequently, the morphology of the iron oxide layer and the valence state of iron depended on the various treatments. The best catalyst activity in CO oxidation was found after oxidative treatment.

The Au/Fe$_2$O$_3$ catalyst prepared by co-precipitation had similar features to the model system. XPS, TEM, electron diffraction (ED) and X-ray diffraction (XRD) studies [12, 13] highlighted the structure of the sample in the as prepared, oxidized and reduced states. The results show the stability of the gold particle size during both the oxidative and reductive treatments. However, after oxidation, a slight shift in the Au 4f binding energy towards lower values points to the formation of an electron-rich state of the metallic gold particles compared to that revealed in the as prepared sample. The goethite phase (the orthorhombic form of the FeO(OH)) is present in the Fe$_2$O$_3$ support, and this was not observed in the as prepared and reduced samples. In the reduced sample the presence of crystalline maghemit-C phase indicates a change in the support morphology. For CO oxidation, the oxidized sample gave the highest activity and this might arise from a cooperative effect between goethite and the electron rich metallic gold nanoparticles, and the maghemite-C phase may cause a significant decrease in activity.

We suggest that a structural transformation occurs along the gold/support perimeter during the treatments and we have proposed a possible mechanism for the effect of the oxidation treatment. The high activity observed for CO oxidation requires both gold nanoparticles and electronic interactions between the gold particles and the support. To obtain high activity we need formation of the oxygen vacancies at metal/support interface and there we need the activation of O$_2$ with the formation of O$_2^-$ species. In the most active state the gold is in the metallic state and the Fe$_2$O$_3$ support contains Fe$_3$O$_4$ in hematite phase, FeO and FeO(OH). Based on a model system, we suggested a mechanism for the effect of oxidation treatment where the O$_2^-$ formed at the interface has a crucial role. This mechanism fits well with relevant literature data. Undoubtedly the oxygen vacancy should be in the vicinity of gold particles as was proved by complementary experiments.

Structural changes can be inferred when using Au-Fe/HY catalyst containing metallic gold and the iron being contained in the zeolite supercages [14]. Iron(II) ethylenediammonium and gold ethylenediamine complexes were used to prepare the Au-Fe system. In the presence of iron the diameter of the gold nanoparticles increased compared to the monometallic Au/HY sample, as indicated by TEM investigations. However, in Au/HY $^{195}$Xe NMR studies revealed the existence of a small proportion of gold ions. The effect of iron lies in the stabilization of gold in Au$^+$ state. In the CO oxidation the Au-Fe/HY catalyst showed the highest catalytic activity.

While the morphology, electron structure and catalytic activity of the Au/Fe$_2$O$_3$/SiO$_2$/Si(100) model (AuPLD), and the co-precipitated Au/Fe$_2$O$_3$ (AuCP) samples in response to the oxygen and the subsequent hydrogen treatments are similar [15] it is reversed for the Au-Fe/HY (AuHY) sample. The difference cannot be ascribed to the change in particle size because the average diameter of gold particles is always in the range 4–6 nm, and is only slightly modified by oxygen/hydrogen treatments. The difference between the samples cannot be ascribed to surface carbon contamination, either, because after oxygen treatment the amount of carbon slightly decreases and this cannot account for the activity increase. The major difference lies in activation at the gold/iron oxide interface, which is well developed in the case of the AuPLD and AuCP catalysts, but does not exist inside the zeolite in the AuHY sample. In the latter case, the O$_2^-$ superoxide which is responsible for the enhanced activity cannot be formed.

The role of interface in the Au/iron oxide system

There is evidence that the role of the gold/oxide interface is crucial in the field of gold catalysis. It was modeled using 10 nm thick gold film deposited onto a SiO$_2$/Si(100) wafer possessing no catalytic activity for CO oxidation. After Ar$^+$ ion implantation (40 keV and 10$^{15}$ at/cm$^2$) gold nanoparticles were created [16]. The intrinsic catalytic activity of the gold particles increased with decreasing size for CO oxidation. The activity of Au nanoparticles/SiO$_2$/Si(100) sample decreased during repeated catalytic runs, caused by the Au sintering and regaining bulk character. However, when Fe$_3$O$_4$ was deposited onto the gold particles, thus creating a gold/oxide interface, higher catalytic activity was again detected in CO oxidation. To verify the “inverse” interface (gold is covered by iron oxide) effect, an oxide layer with a well defined architecture and 5–10 nm thickness was deposited by PLD onto either Au films or nano-sized Au particles supported by SiO$_2$/Si(100) [17]. After appropriate characterization, a comparison was made with reference samples either free of iron oxide and/or free of Au particles/films. Secondary ion mass spectrometry (SIMS) and XPS proved the absence of gold at the surface of the FeO$_x$ covered samples. The initial activity of FeO$_x$/Au nanoparticles/SiO$_2$/Si(100) turned out to be the highest followed by the sample containing a sandwiched Au film. Some reaction-induced changes in the chemical composition of the iron oxide overlayer (FeO$_x$) were seen: these can be regarded as a mixture of Fe$_3$O$_4$, FeO and FeOOH according to an XPS analysis of the Fe 2p and O 1s core levels and no Au segregation at the surface was detected by TOF SIMS. The XPS Au 4f spectra indicated, however, that Au atoms might be injected into and trapped in this layer. The catalytic activity of the FeO$_x$/Au/SiO$_2$/Si(100) samples must be attributed to active sites located on the iron oxide overlayer promoted by gold underneath. Since Au nanoparticles and Au films caused promotion we infer that an electronic effect is in operation due to the occurrence of an FeO$_x$/Au interface in both cases. Since the promotion is stronger for Au nanoparticles, the hypothesis of a particle size dependent electronic effect may be
advanced. For thicker FeOx of about 40–60 nm no promotion by Au was found.

Similar experiments were carried out with the TiO2/Au/FeOx/SiO2(100) system. When TiO2 was evaporated onto a Au/FeOx/SiO2(100) sample the catalytic activity in CO hydrogenation increased, but the reference TiO2/SiO2(100) showed even higher activity. The gold affected the catalytic activity of the TiO2 overlayer in the opposite way to the FeOx/Au system. However, in both cases a significant difference could be observed between the effect of Au-nanoparticles and the bulk type of Au. Gold nanoparticles had a larger effect than the massive 80 nm thick gold layer [18].

We have already expanded our research toward preparation of bimetallic systems (such as Au-Pd) on various supports, mostly using the sol technique [19, 20].

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