An SiO_2-Embedded Nanoscopic Pd/Au Alloy Colloid

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A bimetallic, fully alloyed Pd/Au colloid of 3.0 nm particle size, obtained by the co-reduction of Pd and Au salts with tetraalkylammonium triethylhydroborate, was embedded in a silica matrix employing a modified sol–gel procedure with THF as the solvent. The removal of the protecting tenside led to a mesoporous texture with a comparatively narrow pore distribution. The physical characterisation by a combination of several techniques has shown that the SiO_2-embedded Pd/Au colloid preserves the size and the structural characteristics of the colloidal metal precursor. The new material exhibits catalytic properties in selective hydrogenation.

The incorporation of preformed ligand-stabilized metal clusters and colloids is currently of interest both in basic research[1] and for applications in heterogeneous catalysis.[2a][2b] Bimetallic heterogeneous Pd catalysts have elicited a large interest because of their superior selectivity and their resistance to deactivation which has been observed in several processes of practical importance.[3,4,5] Gold by itself, supported on SiO_2, Al_2O_3 or MgO, shows a rather low catalytic activity,[6] but its addition to Pd was found to lead to an enhanced catalytic activity which has been interpreted in terms of geometric or electronic effects.[7,8]

Most reports on bimetallic Pd catalysts refer to systems prepared via the coimpregnation of the metal salts on solid supports using the incipient wetness technique, followed by calcination.[9,10] However, a vigorous debate is still going on as to whether the resulting Pd–Au particles on the support are fully alloyed.[11] Recent data from a combined XANES and EXAFS study made by Couves and Meeham[12] have emphasized these doubts. Another problem lies in the metal dispersion. There is strong evidence that the addition of Au to Pd salts results in a marked decrease of the dispersion of the bimetallic catalyst systems.[10,13]

Pre-prepared colloidal alloy particles, covered by various protecting shells, offer a different means of access to highly dispersed bimetallic catalyst precursors.[14–19] Following the so called "precursor concept",[20] these pre-prepared nanometals, for which the particle size distribution, composition and structure are rather well defined, may be deposited on various supports to give a new type of heterogeneous bimetallic catalyst.[18–21] Here we report the preparation of a heterogeneous Pd/Au catalyst formed by the embedding of pre-prepared tetraalkylammonium-stabilized Pd/Au alloy particles in a solid SiO_2 matrix following a modified sol–gel process.

The colloidal Pd/Au precursor was prepared in analogy to ref.[18] by the co-reduction of Pd and gold salts with $NOct_4[BEt_3H]$ (= Tetraoctylammonium triethylhydroborate) in dry THF under argon. A solution of palladium acetate (786 mg, 3.5 mmol) and gold chloride (1061 mg, 3.5 mmol) in 300 mL THF was added over the course of 2 h to a vigorously stirred solution of 0.38 M $NOct_4[BET_3H]$ in THF (46.1 mL) at ambient temperature. This process went to completion over the next 16 h and was accompanied by a colour change to black, indicating the formation of colloidal noble metal in solution. The excess of the reducing agent was removed by adding 5 mL acetone to the reaction mixture, which was stirred for another 30 min. The precipitate was removed by filtration and the solvent was evaporated under vacuum (10^{-3} mbar, room temperature, 16 h.). The isolated raw colloidal powder was redispersed in 40 mL diethyl ether and then precipitated by adding 330 mL of an ethanol/methanol mixture, which dissolves any excess protective surfactant. The mixture was allowed to stand for 24 h before the colourless supernatant was removed by decantation. The colloid was precipitated and dried in vacuo. The resulting colloid powder is fully redispersible in THF and has a metal content of 5.28 wt-% Pd and 8.96 wt-% Au (atomic ratio Pd/Au = 53:47). Monometallic Pd and Au colloids were prepared for comparison applying an analogous procedure.[19]

The embedding of the Pd/Au colloid was carried out with tetraethoxysilicate (TEOS) as the precursor for the silica support. However, since the NR_4-stabilized Pd/Au colloids are completely insoluble and even decompose at elevated temperatures in alcoholic solutions, the normal sol–gel procedure has to be modified by using THF as the solvent. The

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molar composition of the sol was TEOS/THF/H_2O/HCl = 1:3.5:4:0.05. The colloid was added as a 4.5 wt-% THF solution at room temperature, after refluxing. The sol was stirred vigorously at 70 °C (under reflux) until the gelification was complete (after 2 days). To avoid any decomposition in the presence of air, all steps were carried out under argon. The resulting gel was dried at 110 °C using a ramp of 0.12 °C min^{-1} then calcined in air at 450 °C with a ramp of 0.3 °C min^{-1}. After cooling, the samples were reduced in flowing hydrogen at 450 °C using the same ramp. For comparison, dried samples were subjected directly to reduction without an intermediate calcination. These samples contained 1 wt-% of metal. Thermal activation (450 °C) of such hybrid materials resulted in a porous texture having a rather narrow pore diameter in the region of the mesoporous materials.

The characterisation of the Pd/Au colloids both in the free and in the embedded state was first performed by transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), and atomic absorption spectroscopy (AAS). In addition, nitrogen adsorption-desorption curves at 77 K, H_2 chemisorption measurements, solid state ^{29}Si NMR, XRD, SAXS, XPS, and ^{197}Au Mössbauer spectroscopy were applied.

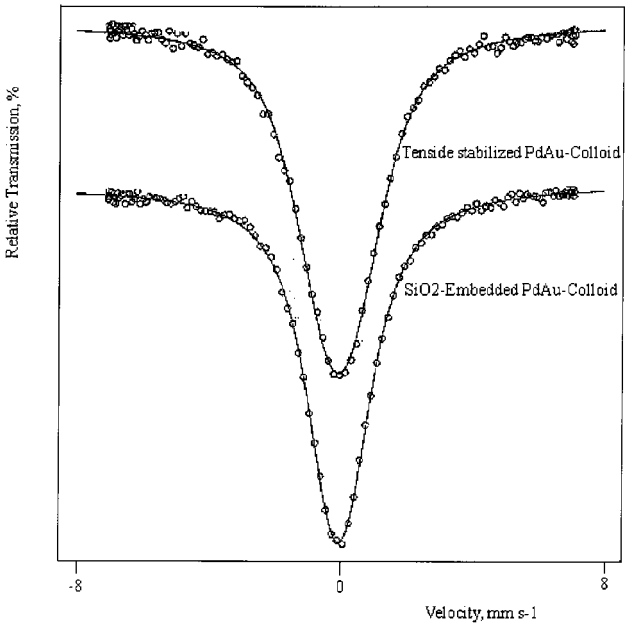

Figure 1. ^{197}Au Mössbauer spectra of tenside-stabilized pure and SiO_2-embedded Pd/Au colloid

Both Mössbauer (see Figure 1) and XRD analyses of the free Pd/Au colloid showed a fully alloyed material consisting of 52% Pd and 48% Au. These values correspond closely to those found by the chemical and EDX analysis. The embedding of the Pd–Au colloids in the sol–gel matrix does not alter the Mössbauer spectrum. There is no difference between the isomer shifts in the free Pd/Au colloid and in the embedded sample, confirming that the colloid structure had not changed during the sol–gel process. The integrity of the incorporated Pd/Au alloy particles remained virtually untouched.

The intensity distributions of XRD patterns of the embedded Au, Pd and Pd/Au colloids correspond to silica and to metallic or bimetallic species. An intense diffraction peak at 22° 2-Θ originates from calcined SiO_2, showing that the support is not totally amorphous. All peaks in the pattern recorded for the bimetallic system containing 1.0 wt-% Pd/Au in SiO_2 correspond to a bimetallic Pd/Au alloy, and no peaks assignable to single Au or Pd species are present. A peak broadening analysis was performed on the basis of FWHM values obtained from peak fitting using a pseudo-Voigt peak shape function. The instrument line broadening was obtained using a standard Si sample. The result indicates a particle size of ca. 3.0 nm both for the Pd/Au and the Au system, whereas the particles in the pure Pd system appear to be larger (ca. 5.6 nm). The composition of the bimetallic Pd/Au alloy was determined from lattice parameter calculations (52 wt-% Au, 48 wt-% Pd; a = 3.976 Å).

Table 1 summarises the textural characteristics of the embedded colloids and the H_2-chemisorption data. The results indicate that in all cases a mesoporous material was present with a rather sharp pore diameter distribution. However, SAXS has shown that the channels are randomly distributed and no tubes (such as those found in MCM materials) are present here. The same information resulted from the TEM analysis. The pore diameter and the mesoporous texture are related to characteristics of the surfactant used. The dispersion of the monometallic Pd colloid in the silica gel matrix was found to be lower than in the case of the bimetallic Pd–Au colloid in the same matrix. For the same metal loading, the Au-containing silica gel matrix exhibited the lowest dispersion. The large differences found between the amounts of physically adsorbed hydrogen and chemisorbed hydrogen, especially for Au, may account for the contribution of the support. TEM measurements (Figure 2) have confirmed a narrow size distribution of the incorporated bimetallic colloid (about 3.0 nm), another proof of the conservation of the characteristics of the colloidal precursor in the incorporated state.

The ^{29}Si CP/MAS NMR spectrum of a Pd/Au SiO_2 sample (1.0 wt-%, preactivated in hydrogen) shows the characteristic structure for Si–O bonds. A ^{29}Si MAS analysis using the "Block decay" procedure indicated that the population of Q^3 species is about 18 %, whereas almost no Q^2 species were found. These data confirm a good polymerisation grade of the silica. The Q^3-to-Q^4 ratio, when compared with published data, was proved to be consistent with the incorporation of the colloids in the silica network.[22] On the basis of the same ^{29}Si MAS analysis it was concluded that the so-called "T surrounding species" are absent.

To test the catalytic properties of the incorporated Pd/Au colloid, we examined the selective semi-hydrogenation of 3-hexyn-1-ol, which gives the corresponding *cis*-hexenol derivative. This is a valuable perfume ingredient.[18] Under standard test conditions, 6.1 mL of 3-hexyn-1-ol were converted without solvent in a stirred 50 mL stainless steel autoclave using 50 mg of catalyst (1 wt-% metal incorporated) at 20 bar hydrogen and 20 °C. The reaction products

Table 1. BET surface area, average pore diameter, hydrogen uptake, metal dispersion, and metallic surface area for the sol–gel-embedded catalysts

Catalyst	BET surface area [$m^2\ g^{-1}$]	Average pore diameter [Å]	Chemisorbed hydrogen			
			H_2 uptake [$cm^3\ g^{-1}$]	Metal dispersion [%]	Metal surface area [$m^2\ g^{-1}_{sample}$]	Metal surface area [$m^2\ g^{-1}_{metal}$]
Pd–SiO_2	319	34	0.30	14.25	0.63	63.2
Au–SiO_2	281	34	0.08	7.38	0.18	17.8
Pd/Au–SiO_2	292	35	0.48	27.60	1.01	101.2

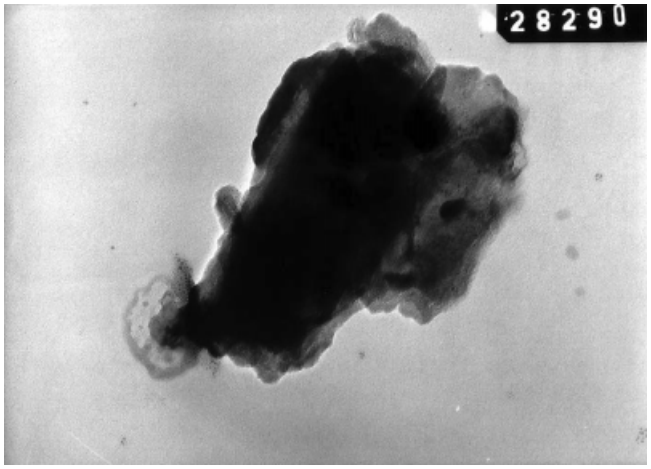

Figure 2. TEM of SiO_2-embedded Pd/Au colloid

were analysed by GC using a Varian 3700–519 chromatograph equipped with a 50 m CW-20M column. The reaction products were identified using the same GC coupled with a Finnigan MAT SSQ7000 mass spectrometer on the basis of pure standards. The results are shown in Figure 3.

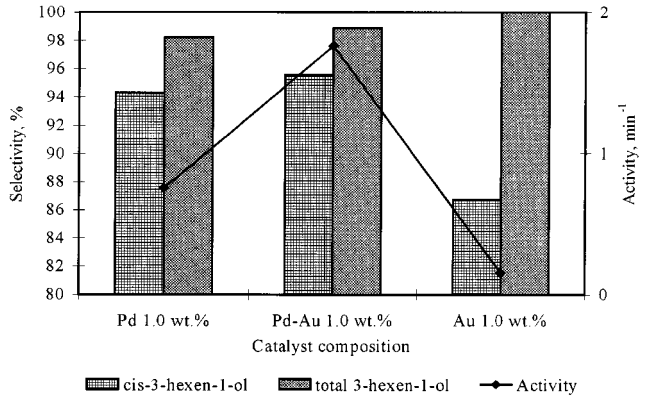

Figure 3. Catalytic activity and selectivity of the embedded colloids in the hydrogenation of 3-hexyn-1-ol

An inspection of Figure 3 shows that the catalytic activity is lowest for the embedded-Au-catalyst sample. As we expected, the catalytic activity of incorporated Pd/Au particles in SiO_2 proved to be superior to monometallic samples. Hexenol and hexanol were the only reaction products. The chemoselectivity towards hexenol reached 100% in the case of embedded Au colloids. Both the other catalysts yielded hexenol and hexanol, the chemoselectivity to hexenol still exceeding 95 %. Both the monometallic Pd and the bimetallic Pd/Au catalysts exhibit a high *cis* selectivity (> 95 %). The performances of the bimetallic Pd/Au catalyst are similar to the highest level reported in the literature.[18] Figure 4 shows the time evolution of the conversion. The selectivity in all the recorded points accounts for the values presented in Figure 3.

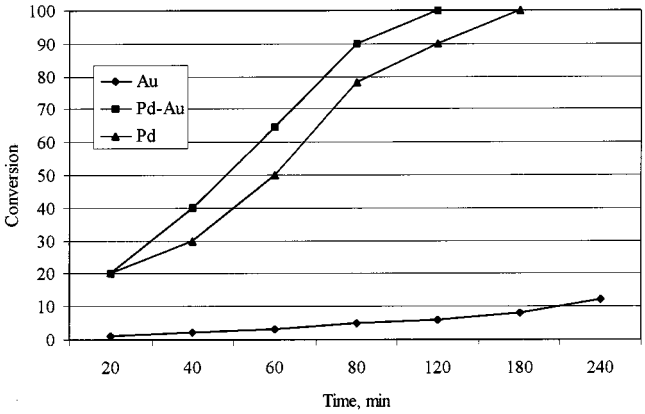

Figure 4. Time evolution of the conversion

Furthermore, we have found that bimetallic Pd–Au colloids incorporated in SiO_2 by sol–gel techniques are active catalysts for selective C,C hydrogenations of unsaturated substrates, e.g. of cinnamaldehyde and styrene. In addition SiO_2-embedded nanoscopic Pd/Au catalysts under these conditions are remarkably resistant to deactivation.

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