Catalytic Properties of Layered Gold–Palladium Colloids

Günter Schmid,* Heike West, Jan-Olle Malm, Jan-Olov Bovin, and Carl Grenthe

Dedicated to Professor Max Herberhold on the occasion of his 60th birthday

Abstract: Layered bimetallic gold–palladium colloids in the size range of 20–56 nm have been synthesized by the seed-growth method: gold seeds were covered by palladium layers of various thickness and vice versa. The outer metal was coordinated by trisulfonated triphenylphosphine and sodium sulfanilate ligands to stabilize the bimetallic particles to such an extent that they could be isolated in the solid state. Owing to the hydrophilic ligand shell, redispersion in water was possible in any concentration. High-resolution transmission electron microscopy and energy-dispersive X-ray analysis was used to characterize the colloids. Stabilized and nonstabilized gold–palladium and palladium–gold systems on a TiO_2 support were used as heterogeneous catalysts for the hydrogenation of hex-2-yne to *cis*-hex-2-ene. Both the palladium-plated gold seeds and the gold-plated palladium particles showed considerably increased activities compared with the pure metals. The ligand shell seems not to influence the catalytic behavior because protected and unprotected colloids behave very similarly.

Keywords
catalysis · colloids · gold palladium colloids · HRTEM · hydrogenations

Introduction

Alloy-like gold–palladium colloids have played an important role in the study of the mutual influence of two different metals with respect to catalytic properties. Owing to their similar atomic radii and crystal structures, gold and palladium are miscible in any ratio. However, electronically, Au–Pd alloys behave differently from the pure metals. The combination of the partially filled d band of Pd and the completely filled d band of Au on the one hand, and the different electronegativities on the other hand, gives a novel electronic structure, which may be responsible for the frequently observed unique catalytic behavior of Au–Pd alloys. Numerous papers have reported evidence for such properties.[1–10]

In contrast to the alloy-like systems, bimetallic particles with layered structures have been much less widely investigated. Colloids, consisting of a core of metal 1 and a surrounding layer of a second metal 2 of varying thickness (Fig. 1), are well-suited for the study of intermetallic behavior from different points of view. For instance, they can serve as models for alloy formation;[11,12] they are also useful aids for understanding electronic interactions, and are better in this respect than alloy-like systems.

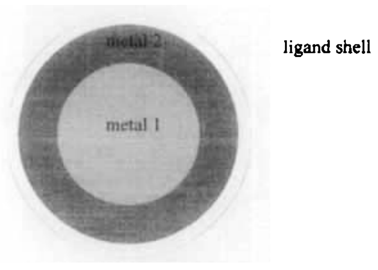

Fig. 1. Model of a ligand-stabilized, layered bimetallic colloid.

We have developed a method of stabilizing layered bimetallic colloids by means of chemically bonded ligand molecules, which allows them to be handled as solid but redispersable materials.[13] Owing to the thin but well-fixed ligand shell, coalescence processes between colloidal particles are prevented without using polymers. Colloids embedded in a matrix of polymeric material are only available as liquids or as oily systems with low metallic content. In contrast, ligand-stabilized colloids usually consist of more than 90% metal.

Gold-plated palladium colloids were described by Turkevitch et al. as far back as 1970.[14,15] The palladium–gold system was later elaborated in all three possible combinations: as a homogeneous alloy, as palladium-plated gold, and as gold-plated palladium.[16] Layered Au/Pd and Pd/Au[+] colloids can be prepared by the so-called seed-growth method: a hydrosol of metal 1 is prepared by reduction of its cation with sodium citrate. In a second reduction step, metal 2 is grown on metal 1 with hydroxylamine as reducing agent. The seed-growth mechanism has been known since 1906,[17] when 15–20 nm gold colloids were enlarged to 30–40 nm in a second reduction step. The diameter of the resulting particles, d_{res}, is controlled by the number of seeds [Eq. (1)],[18] where d_0 is the diameter of the seeds of

$$d_{res} = d_0\sqrt{(n_i + n_m)/n_m} \qquad (1)$$

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[+] Au/Pd is used for colloids consisting of a gold core plated by palladium, and Pd/Au for a palladium core plated with gold. Additional numbers indicate the diameter (nm) of the core and of the whole colloid particle, e.g., Au/Pd 18/25.

metal 1, n_i is the molar amount of ionic metal 2, and n_m is the molar amount of metal 1 colloids. The formula indicates that the thickness of the metal 2 layer can be modified in a wide range, which will be of importance for the study of the mutual electronic influence.

Suitable stabilizing ligands for Au/Pd and Pd/Au colloids are, in principle, the same ligands used in complex chemistry or to protect the corresponding monometallic colloids. Trisulfonated triphenylphosphine (TPPTS) $[P(m\text{-}C_6H_4SO_3Na)_3]$ gives perfect protection to colloidal gold surfaces, whereas $p\text{-}H_2N\text{-}C_6H_4SO_3Na$ stabilizes monometallic palladium colloids.[13] Thin layers of Pd on Au are best stabilized by TPPTS, whereas thicker Pd layers on Au are best protected by a molar 1:1 mixture of sulfanilate and phosphine.

The aim of the present paper is to show how the combination of two metals in a bimetallic layered colloid (Fig. 1) influences the electronic behavior of the inner and outer metals. In addition, it is to be expected that the molar ratio of metals 1 and 2 contributes to the extent of electronic interchange. Since the thickness of metal 2 can vary from a few atomic layers to a few nanometers, it should be possible to study the influence of the inner metal on the outer metal layer as a function of the latter's thickness.

In contrast to homogeneously mixed bimetallic colloids, the catalytic properties of Au/Pd layered bimetallic particles can best be viewed as resulting from the electronic band-gap energy. An alloy-like colloid would certainly have a very different band-gap energy. The contact between two metals, differing not only in their electron configurations but also in their electronegativities, unavoidably causes electron transfer processes from the electropositive to the electronegative metal. Such electron shifts can be observed by means of UV/Vis spectroscopy. An increase in electron density causes a blue shift of the plasmon resonance, whereas a red shift indicates a reduction in electron density. For instance, silver layers on 6 nm colloidal Au particles shift the Au plasmon absorption band to considerably shorter wavenumbers, whereas the absorption band of silver is red-shifted.[17] A similar behavior is found in Pb-plated Au particles, due to the electron transport from the electropositive lead to the electronegative gold.[19] The UV/Vis spectra of the gold–palladium colloids described in this paper agree with these findings and will be described in detail together with other optical properties.

Abstract in German: *Schalenförmige bimetallische Gold-Palladium-Kolloide im Größenbereich von 20–56 nm werden mit Hilfe der Keim-Wachstumsmethode synthestisiert: Gold-Keime werden durch Palladium- und Palladium-Keime durch Gold-Lagen unterschiedlicher Dicke belegt. Das äußere Metall wird durch trisulfonierte Triphenylphosphan- und Natriumsulfanilat-Liganden koordiniert, um die dimetallischen Teilchen so zu stabilisieren, daß sie im festen Zustand isoliert werden können. Aufgrund der hydrophilen Ligandhülle ist eine Redispergierung in Wasser in beliebiger Konzentration möglich. Die Kolloide werden mit hochauflösender Transmissionselektronenmikroskopie und energiedispersiver Röntgen-Analyse charakterisiert. Stabilisierte und nichtstabilisierte Gold-Palladium- und Palladium-Gold-Systeme werden auf TiO_2 als Träger als heterogene Katalysatoren für die Hydrierung von Hex-2-in zu cis-Hex-2-en verwendet. Nicht nur die palladiumbelegten Goldkeime, sondern auch die goldbeschichteten Palladium-Teilchen sind beträchtlich aktiver als die reinen Metalle. Die Ligandhülle scheint das katalytische Verhalten nicht zu beeinflussen, da sich geschützte und ungeschützte Kolloide sehr ähnlich verhalten.*

Results and Discussion

Following the procedure described in reference [13], various Au/Pd colloids were prepared, based on 18 nm Au seeds plated with Pd layers of different thickness. This was controlled by changing the amount of H_2PdCl_4 used in the reduction with hydroxylamine. As mentioned above, instead of sulfanilate, TPPTS or a mixture of both ligands was used for stabilization. The Pd/Au colloids were prepared by a similar method to that outlined above. Based on 20 nm Pd seeds, which were obtained by the citrate method, gold layers were added by reduction of $HAuCl_4$ with hydroxylamine. Three Au/Pd and three Pd/Au colloids were studied. Energy-dispersive X-ray (EDX) analysis, which was used as an additional method to high-resolution transmission electron microscopy (HRTEM) for the characterization of the bimetallic colloids, not only revealed the shell structure, but also its composition and size; the composition was found to be in good agreement with calculated values. Table 1 summarizes the EDX analysis of the colloids. Figures 2 and 3 show HRTEM images of Au/Pd 18/25 and Pd/Au 20/30 colloids as typical examples of the colloids studied here.

Catalytic Properties of Au/Pd and Pd/Au Colloids: It is known from experiment that metal colloids normally do not survive several catalytic cycles in "solution". Their catalytic stability can be increased by immobilization on suitable supports. The catalytic properties of palladium can best be examined by means of its hydrogenation reactions. Here, the partial hydrogenation of hex-2-yne to *cis*-hex-2-ene was chosen to investigate activity

Table 1. EDX and calculated compositions of various Au/Pd and Pd/Au colloids.

Colloid, core size/ total size (nm)	EDX analyses (atomic%)	Calculated (atomic%)
Au/Pd 18/20	69±1:31±1	72.9:27.1
Au/Pd 18/25	41±5:59±5	37.3:62.7
Au/Pd 18/30	19±2:81±2	21.6:78.4
Pd/Au 20/24	71±5:29±5	68.7:31.3
Pd/Au 20/30	44±7:56±7	42.2:57.8
Pd/Au 20/56	15±3:85±3	12.5:87.5

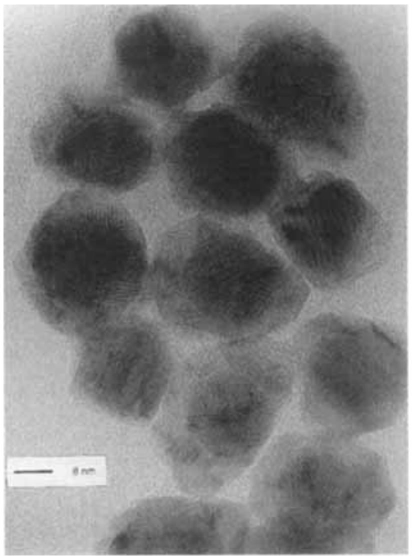

Fig. 2. HRTEM image of gold–palladium colloids consisting of a 18 nm Au core (dark area) and a ca. 4–5 nm thick Pd shell.

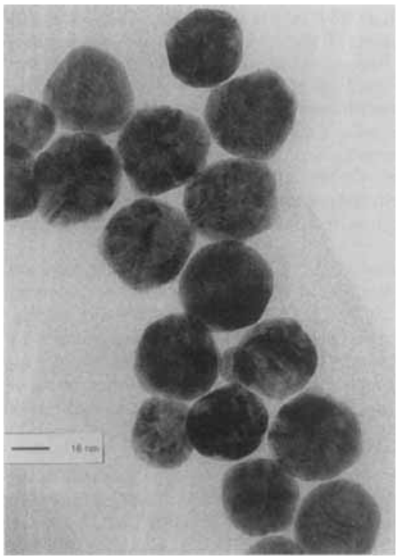

Fig. 3. HRTEM image of palladium-gold colloids. The core/shell structure was confirmed by EDX. The 20 nm Pd core appears as a brighter patch in some of the particles. The average total diameter is 35 nm.

as well as selectivity. Large ligand-stabilized Pd clusters, in the size range of 3.0-3.6 nm, are highly reactive; the selectivity is influenced by the ligand shells.[20, 21]

Both ligand-stabilized and "nonstabilized" colloids, which are in fact weakly stabilized by the species present in the original solution, were used for the semihydrogenation of hex-2-yne on TiO_2. The results with ligated and nonligated colloids showed that the ligands do not exert any characteristic influence. In some cases the activity was somewhat reduced when the strong phosphine and sulfanilate ligands covered the surface. The effect studied here is therefore the electronic interchange between gold and palladium. Table 2 presents the colloids used for the semihydrogenation of hex-2-yne. The pure metallic Au and Pd colloids were tested under analogous conditions for comparison. As a representative example of the catalysts summarized in Table 2, the results of a typical catalytic reaction are shown in Figure 4. The different catalysts differ remarkably in activity, but only slightly in selectivity. The selectivity for *cis*-hex-2-ene is found to be between 90-99%.

Table 2. Catalysts used for the semihydrogenation of hex-2-yne to *cis*-hex-2-ene. Colloids stabilized phosphine and sodium sulfanilate ligands are indicated by P and N, respectively. All catalysts contain 0.5 wt% of metal on TiO_2.

Catalyst	Au:Pd/wt%	Catalyst	Au:Pd/wt%
Au 18	100:0	Au/Pd 18/30 P,N	34:66
Pd 20	0:100	Au/Pd 18/36	21:79
Pd 20 N	0:100	Au/Pd 18/36 P,N	21:79
Au/Pd 18/25	52:48	Pd/Au 20/24	54:46
Au/Pd 18/25 P	52:48	Pd/Au 20/30	28:72
Au/Pd 18/30	34:66	Pd/Au 20/56	7:93

The catalytic reactions were carried out under standard conditions: 1 g of the catalyst, containing 0.5 wt% metal, was dispersed in 10 mL ethanol. The 2 mL of hex-2-yne was added and hydrogenated with gaseous hydrogen from a gas burette, at room temperature with stirring. The measured activities are shown in Figures 5 and 6.

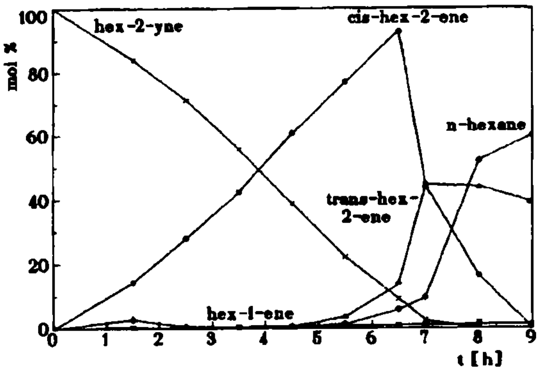

Fig. 4. Course of the semihydrogenation of hex-2-yne to *cis*-hex-2-ene with 0.5 wt% Au/Pd 18/30 P,N on TiO_2 (1 g catalyst, 2 mL) hex-2-yne, 10 mL) ethanol, room temperature, 1 atm H_2).

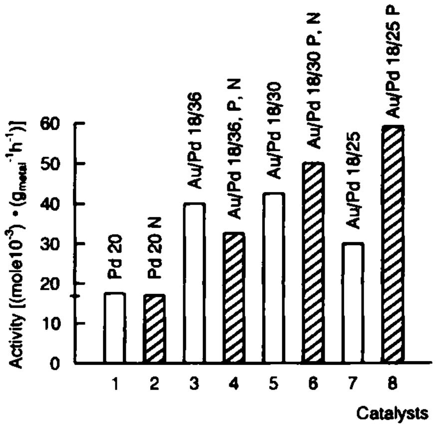

Fig. 5. Hydrogenation of hex-2-yne to *cis*-hex-2-ene. Activities of various stabilized and nonstabilized Pd and Au/Pd colloids on TiO_2. Conditions as described in Fig. 4. Shaded columns indicate stabilized colloids.

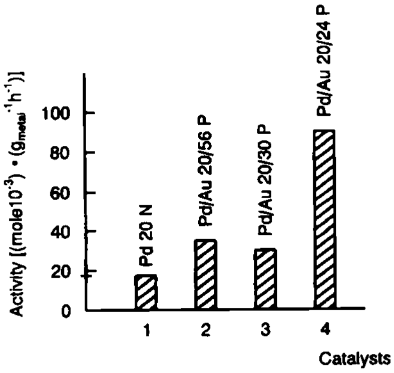

Fig. 6. Hydrogenation of hex-2-yne to *cis*-hex-2-ene. Activities of various stabilized Pd and Pd/Au colloids on TiO_2. Conditions as described in Fig. 4.

As can be seen from Figure 5, stabilized as well as nonstabilized monometallic Pd colloids show the lowest activities, followed by the colloids with the thickest Pd shell. The activity increases via the Au/Pd 18/30 species to a maximum for the ligand-stabilized Au/Pd 18/25 P catalyst. The data indicate that the gold core influences the palladium shell substantially (or vice versa) and that this influence increases with decreasing thickness of the Pd layer. A clear systematic difference between stabilized and nonstabilized colloids cannot be observed. The explanation for these findings is not clear. It might be expected that ligand-stabilized colloids would be less active than the nonstabilized ones. In the case of the Au/Pd 18/25 colloids the opposite effect is even observed (Fig. 5). One possible explanation is that the N and P ligands do not cover the total surface of a colloidal particle. As for ligand-stabilized palladium clusters,[20, 21] there are enough free surface atoms for fast catalytic steps. For instance, oxygen is removed during hydrogenation reactions, and active sites are thus generated. On the other hand, the "nonstabilized" colloids must also be considered to be covered by various ions and molecules from the solution used in their preparation, which cannot completely be removed during the absorption process.

Although the results might have been expected, monometallic ligand-stabilized Au18 colloids were tested and found to be completely inactive. This eliminates errors that might have been caused by impurities of Au colloidal particles not plated with Pd. The gold in Au-plated Pd colloids is thus expected not to be catalytically active. The catalytic activity must result from the combination of the two metals. There is a clear increase in catalytic activity on going from pure palladium to the 20 nm Pd core covered with very thick gold layers (Fig. 6). The colloid Pd/Au 20/24 with the thinnest Pd layer (2 nm) shows the highest activity. It cannot be excluded that the thin-plated Pd colloids are only partially covered with Au and thus offer free Pd sites for catalysis. As the activity of pure Pd is lower, however, such defects should not contribute to the increase in the observed activity, as even thick-plated Pd colloids show increased activities compared with pure Pd.

Lifetime tests on a few catalysts indicate that the ligand-stabilized colloids are more stable than the unprotected ones. For instance, in the case of Au/Pd 18/36 P,N the activity was the same after four cycles, whereas the activity of the unprotected species decreased to around 50 % of the original value. It may be that the lifetime is being shortened by coalescence processes, which are prevented by the presence of the ligand shells. The lifetime of the gold-plated palladium colloids is considerably shorter. Depending on the thickness of the gold layers, the activity decreases dramatically: from 90 to 0.8 for Pd/Au 20/24 P, from 30 to 3.1 for Pd/Au 20/30 P, and from 34 to $0.8\,\mathrm{mmol\,g_{metal}^{-1}\,h^{-1}}$ for Pd/Au 20/56 P. HRTEM studies before and after the catalytic cycles would help to clarify this question and are part of a current project.

Experimental Procedure

As the synthesis of mixed Au/Pd and Pd/Au colloids, stabilized by various ligand molecules, has only been described very briefly in a communication [13], the synthetic procedures will be given here in detail.

Starting materials: H_2PdCl_4 was prepared following a literature procedure [22] from $PdCl_2$ (6.60 g), dissolved in HCl (800 mL 1 N), diluted to 1 L by completely desalinated water. A solution with a Pd concentration of $3.96\,\mathrm{g\,L^{-1}}$ was obtained. $HAuCl_4$ was prepared as described in ref. [23] by dissolving gold metal in aqua regia, repeatedly evaporating with conc. hydrochloric acid and dissolution in desalinated water. The concentration of Au was $5.0\,\mathrm{g\,L^{-1}}$. $P(C_6H_4SO_3Na)_3 \cdot 6H_2O$ was obtained by using a modified patent [24,25] by reaction of $P(C_6H_5)_3$ with oleum. $H_2NC_6H_4SO_3Na$ is commercially available.

Gas chromatography: DANI 8520 with flame ionization detector; SHIMADZU C-R5A integrator; PONA capillary column (cross-linked methyl silicone gum) 50 m × 0.2 mm × 0.5 µm film thickness, external standards.

High-resolution transmission electron microscopy: For the electron microscopy work a JEM-4000 EX machine operated with an accelerating voltage of 400 kV was used.. This instrument has a proven structural resolution of 0.16 nm. The EDX analyses were performed using a Link-AN-10000 system, coupled to a JEM-2000-FX-STEM microscope.

Synthesis of the colloids: All glassware was carefully cleaned before use by 1) chromosulfuric acid, 2) desalinated H_2O, 3) boiling aqua regia, and 4) desalinated H_2O.

18 nm gold colloids: Desalinated H_2O (1600 mL) in a 2 L beaker was heated to its boiling point. A 1 % $HAuCl_4$ solution ($5.0\,\mathrm{g\,L^{-1}}$ Au) (16 mL) and a 1 % trisodium citrate solution (80 mL, $10.0\,\mathrm{g\,L^{-1}}$ citrate $\cdot 6H_2O$) were added under vigorous stirring. The reaction was completed after 1 h at boiling point. For the stabilization the red solution was cooled to room temperature and $P(C_6H_4SO_3Na)_3 \cdot 6H_2O$ (50 mg) was added. The water was evaporated in a rotary evaporator at 60 °C and 10 Torr until coagulation began. The precipitate was separated by centrifugation (5000 revolutions per minute). Addition of a few mL of water (only part of the solid material should remain undissolved) and centrifugation yielded ca. 80 mg of golden metallic-looking colloids which can be redispersed in desalinated water giving a dark red color.

20 nm palladium colloids: Desalinated water (3 L) in a 4 L round-bottom flask was heated to its boiling point. $PdCl_2$ solution (15 mL, 3.7×10^{-2} M) and a trisodiumcitrate solution (60 mL, $200\,\mathrm{g\,L^{-1}}$ citrate $\cdot 2H_2O$, 0.68 M) were added with stirring. The reaction mixture was refluxed for 24 h. The stabilization was performed by addition of sodium sulfanilate dihydrate (0.5 g). Concentration by means of a rotary evaporator until coagulation, followed by centrifugation yielded ca. 60 mg of silver-colored solid Pd colloid, which can be redispersed in water to give dark brown solutions.

Bimetallic gold–palladium colloids: Nonstabilized gold colloid, prepared as described above, was used as the nucleation agent. The original 1.6 L of red dispersion was diluted to 8 L in a 10 L beaker. Diluted solutions of H_2PdCl_4 and hydroxylamine hydrochloride were added simultaneously with vigorous stirring over 8 h. Examples of the amounts of Pd and reducing agent used to generate the colloids Au/Pd 18/20, 18/25, and 18/30 are given in Table 3. H_2PdCl_4 and $[H_3NOH]Cl$ were each diluted with H_2O (0.5 L) before use. The reaction mixture was stirred for another 48 h at room temperature. The stabilization of the 20 and 25 nm colloids was achieved by addition of $P(C_6H_4SO_3Na)_3 \cdot 6H_2O$ (0.2 g). Colloids with thicker Pd layers were stabilized with a mixture of the phosphine (0.2 g) and $H_2NC_6H_4SO_3Na \cdot 2H_2O$ (2.0 g). The solid materials were isolated as described for the monometallic species. The solid Au/Pd 18/20 colloid was bronze-colored, the others looked like the Pd colloids.

Table 3. Experimental data for the preparation of Au/Pd colloids.

Colloid	H_2PdCl_4/mL [a]	mmol	1 % $[H_3NOH]Cl$/mL
Au/Pd 18/20	4.0	0.151	10
Au/Pd 18/25	18.1	0.682	25
Au/Pd 18/30	39.2	1.47	50

[a] Volume of original solution with $3.96\,\mathrm{g\,L^{-1}}$ Pd.

Bimetallic palladium–gold colloids: The nonstabilized 20 nm Pd colloid solution, prepared as described above, was used for nucleation. It was diluted to 8 L in a 10 L beaker. Over 10 h, solutions of $HAuCl_4$ and $[H_3NOH]Cl$, each diluted with H_2O (0.5 L), were added simultaneously. After 48 h of vigorous stirring $P(C_6H_4SO_3Na)_3 \cdot 6H_2O$ (0.5 g) was added before isolation as described for the gold colloids. The required amounts of $HAuCl_4$ and $[H_3NOH]Cl$ for three colloids are given in Table 4.

Table 4. Experimental data for the preparation of Au/Pd colloids.

Colloid	$HAuCl_4$/mL [a]	mmol	1 % $[H_3NOH]Cl$/mL
Au/Pd 20/24	10.0	0.254	20
Au/Pd 20/30	30.1	0.765	50
Au/Pd 20/56	154.0	3.91	200

[a] Volume of original solution with $5.0\,\mathrm{g\,L^{-1}}$ Au.

Preparation of catalysts: The catalysts with ligand-stabilized colloids were prepared from isolated colloidal material dissolved in ca. 1 L desalinated water. The corresponding amount of TiO_2 was added, and the mixture stirred until the solution became colorless. The catalyst was separated and dried under vacuum. The catalysts with nonstabilized colloids were prepared from the original solutions in an analogous manner.

Hydrogenation of hex-2-yne: All hydrogenation reactions were carried out under standard conditions. A 25 mL round-bottom flask, charged with the catalyst (1 g) and a magnetic stirrer, was connected with a 4 L gas burette with a flask to balance the pressure. The flask was closed by a septum, and the system filled with hydrogen. Ethanol (10 mL) and hex-2-yne (2 mL) were injected through the septum, which was also used to remove samples for gas chromatography during the hydrogenation. For the lifetime tests the catalyst was separated from the reaction mixture by centrifugation and was used for another cycle without further cleaning.

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