New Au(0) Sols as Precursors for Heterogeneous Liquid-Phase Oxidation Catalysts

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New Au(0) sols were obtained by reducing auric compounds ($AuCl_3$, $NaAuCl_4$, and $HAuCl_4$) with reducing compounds ($H_2C_2O_4$, $SnCl_2$, and $NaBH_4$) in the presence of protective agents [polyvinylalcohol, PVA, and poly(diallyldimethylammonium chloride), PDDA] in aqueous solutions. The sols, characterized by TEM microscopy and UV–visible spectroscopy, consisted of nanoparticles of different sizes depending on the preparation method. The colloidal solutions were immobilized on activated carbon and titania. The obtained heterogeneous catalysts were tested in the selective liquid-phase oxidation of ethylene glycol to glycolate ($pO_2 = 300$ kPa, $T = 343$ K, r.t. = 1 h, [EG] = 0.5 M, EG/Au = 1000, EG/NaOH = 1, EG = ethylene glycol). A comparison of the catalytic activity underlines the importance of using the correct sol with respect to the support. © 2002 Elsevier Science (USA)

INTRODUCTION

The importance of Au(0)-based catalysts is documented by the successful results of the reduction of nitrogen oxides (1, 2), epoxidation of propene (3, 4), and low-temperature oxidation of CO or liquid-phase oxidation of alcohols (5–8). The catalytic activity is strictly related to the preparation methods of highly dispersed, small gold particles, as reported in the literature (9–15, and references therein). The method of gold sol immobilization is a recently introduced alternative procedure and is now an established technique that can be applied to many supports (16–22). Colloidal gold formation in aqueous solution is well known (23, 24, and references therein) and is usually performed by reduction of $HAuCl_4$ (25). For those systems, Turkevich *et al.* reported that particle dimension, size distribution, growth rate, and stability depend on the preparation method (26). Synthetic procedures for producing gold sols consisting of nanoparticles (2–100 nm) and their importance in immunocytochemical techniques have been reviewed (27–29), as well the development of recent nanotechnologies (30–34).

The mechanism of gold particle formation in the sol has also been reevaluated, demonstrating that in the reaction with citric acid large gold particles form early and then shrink as the reaction proceeds (35). This was not observed in other studies (20).

Having extended our research on gold-sol-supported catalysts, we now, in this paper, present novel gold colloid preparations, planned for the generation of heterogeneous catalysts. Three gold precursors ($AuCl_3$, $NaAuCl_4$, and $HAuCl_4$) were used with the reducing agents, $H_2C_2O_4$ and $SnCl_2$, in the presence of stabilizers, which help prevent agglomeration. A polymer (polyvinylalcohol, PVA) and a cationic polymeric surfactant [poly (diallyldimethylammonium bromide), PDDA] were compared. The sols were characterized by UV and TEM measurements and were immobilized on activated carbon or titania that was used as a representative oxide. The heterogeneous catalysts were tested in the selective liquid-phase oxidation of ethylene glycol to glycolate ($pO_2 = 300$ kPa, $T = 343$ K, r.t. = 1 h, [EG] = 0.5 M, EG/Au = 1000, EG/NaOH = 1, EG = ethylene glycol) (16, 17).

EXPERIMENTAL

Materials

$AuCl_3$ (99.99%, Aldrich), $NaAuCl_4 \cdot 2H_2O$ (99.9%, Aldrich), PVA (98% hydrolyzed, average $M_r 13$–23×10^3; Aldrich), PDDA (20 wt% in H_2O, average $M_r 4$–5×10^5; Aldrich), TiO_2, purchased from Degussa (P25, SA = 49 m²/g, 80% anatase), activated carbon from Carbosorb (MK, SA = 900–1100 m²/g, PV = 1.5 ml/g, pH = 9–10), ethylene glycol (99.5%, Fluka), glycolic acid (99%, Fluka), and propionic acid (99.99%, Fluka) were used as purchased. Gold foil (1-mm wide, 99.999%) was purchased from Aldrich. $H_2C_2O_4 \cdot 2H_2O$ (99%, Fluka), $SnCl_2$ (99.9%, Fluka), $NaBH_4$ (96%, Fluka), and NaOH (99.9%, Aldrich) were stored in a desiccator. Gaseous oxygen (99.99%) was purchased from Siad. Milli-Q water was used in all the preparations.

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TABLE 1

Experimental Parameters for the Syntheses of Sols

Au(III)[a]/PVA[b]/H$_2$C$_2$O$_4$[c]	PVA/Au[e] = 0.25–1 H$_2$C$_2$O$_4$/Au[f] = 3–9 Red-violet
Au(III)[a]/PVA[b]/SnCl$_2$	PVA/Au[e] = 0.15–1 SnCl$_2$/Au[f] = 3–10 Light brown, red-brown
Au(III)[a]/PDDA[d]/NaBH$_4$	PDDA/Au[e] = 0.15–1 NaBH$_4$/Au[f] = 2–15 Red

[a] $[Au(III)] = 5.0 \times 10^{-4}$ M.
[b] $[PVA] = 20$ μg/ml.
[c] Reactions thermostatted at 60°C under N$_2$. Sol was obtained after 10 min.
[d] $[PPDA] = 10$ μg/ml.
[e] Wt/wt ratio.
[f] Mol/mol ratio.

Gold Sol Preparation

A HAuCl$_4$ 5×10^{-4} M aqueous solution was obtained by dissolving 10.0 mg of a gold foil in a minimum amount of a 3 : 1 (vol/vol) mixture of concentrated HCl and HNO$_3$, evaporated, and then diluted to 100 ml with Milli-Q water. The 5×10^{-4} M aqueous solutions of NaAuCl$_4$ and AuCl$_3$ were prepared in Milli-Q water and stored for a maximum of 2 weeks. The aqueous solutions of PVA (2% wt/wt), PDDA (1% wt/wt), H$_2$C$_2$O$_4$ (0.1 M), NaBH$_4$(0.1 M), and SnCl$_2$ (0.1 M) were freshly prepared. All solutions were filtered off through a cellulose nitrate membrane (0.2 μm).

General procedure (see also Table 1). The desired volume of an aqueous solution of a stabilizing agent ([PVA] or [PDDA] = 15–100 μg/ml) was added to a yellow aqueous solution of an Au(III) precursor (30 ml, [Au(III)] = 5.0×10^{-4} M). The amount of the reducing agent ($1–8 \times 10^{-3}$ M) was added quickly, under vigorous magnetic stirring, resulting in a colored sol in few minutes.

Gold Sol Immobilization

The sols were immobilized by dipping the support in the colloidal solution. The support amount was calculated so that the final gold loading was 1 wt%. The slurry was magnetically stirred for 2 h and filtered off, and the absorption checked by ICP analyses of the filtrate. If necessary, the pH value of the sols was modified before immobilization; for activated carbon it was adjusted to 2 (by adding concentrated HCl), while in the case of TiO$_2$ the pH was set at 14 by adding a 37% (wt/wt) NaOH aqueous solution. The supported catalysts were rinsed with large amounts of distilled water, and their water content was determined by drying the samples for 4 h at 150°C in air. In contrast to Au/TiO$_2$, Au/C was used wet.

Oxidation Procedures

The catalytic liquid-phase oxidation of ethylene glycol (5 mmol) was carried out for 1 h in basic aqueous medium (5.1 mmol NaOH, total volume of 10 ml) with a substrate/Au molar ratio equal to 1000, at an O$_2$ pressure of 300 kPa and at 373 K. Experimental procedures and quantitative analyses were performed as reported in Ref. (17).

Measurements and Analyses

UV spectra were measured on an HP 8453 spectrophotometer using 150 μl of the sol (0.1-cm quartz cuvette). Samples of sols were deposited on Ni grids (coated with a 2% Formvar film); TEM analyses were carried out with a JEOL 1200 EX electronic microscope. X-ray diffraction experiments were carried out with a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu $K\alpha$ radiation, equipped with a graphite monochromator in the diffracted beam. The gold crystallite sizes were estimated from the peak half-widths using Scherrer's equation with corrections for instrumental line broadening. XPS measurements were performed in an M-Probe Instrument (SSI) equipped with a monochromatic Al $K\alpha$ source with a spot size of 200×750 μm and a pass energy of 25 eV, providing a resolution of 0.74 eV. The quantitative determinations of gold present in the filtrate of the supported catalysts were carried out by ICP–OES measurements on a Jobin Yvon (model 24) instrument. The content of Au(0) supported on TiO$_2$ or activated carbon was assayed by a Perkin–Elmer 3100 Atomic Absorption Instrument. The Au/TiO$_2$ solid was treated with a 3 : 1 (vol/vol) mixture of concentrated HCl and HNO$_3$, producing a yellow solution of AuCl$_4^-$; then TiO$_2$ was filtered off and the filtrate concentrated and diluted with Milli-Q water. The Au/C samples were heated with a 5 : 1 (vol/vol) mixture of concentrated HNO$_3$and H$_2$SO$_4$ till carbon was burnt off. Then a 3 : 1 (vol/vol) mixture of concentrated HCl and HNO$_3$ was added for the transformation of Au(0) into AuCl$_4^-$; the yellow solution was then concentrated and diluted with Milli-Q water. This procedure was also carried out on the used catalysts: no leaching of gold was detected.

RESULTS AND DISCUSSION

Au(0)/H$_2$C$_2$O$_4$/PVA System

The nature of the Au(III) precursors had a negligible effect on the formation of particles, and similar red-violet colloids were obtained for all three gold compounds. An environmentally friendly reducing agent, such as H$_2$C$_2$O$_4$, was used together with PVA at 60°C under N$_2$. PVA stabilizes the gold sol particles by steric repulsion (29). The UV spectra of the sols showed a plasmon resonance peak between 520 and 525 nm, attributable to gold(0) nanoparticles (36). High extinction molar values (ε = 3500–3850 L mol^{-1} cm^{-1}) and TEM analyses proved the presence of polydispersed sols (mean particle diameters of various samples were 5.9–17.6 nm), caused by a slow reduction by H$_2$C$_2$O$_4$, which favors further nucleation. The polydispersion of sols

TABLE 2

Au(III)/H₂C₂O₄/PVA System

Precursor	AuCl₃	NaAuCl₄	HAuCl₄
H₂C₂O₄/PVA[a]	7	7	7
PVA/Au[b]	0.45	0.45	0.45
TOF[c]	130	270	300
d (nm)[d]	9	6	13

[a] Molar ratio.

[b] Wt/wt ratio.

[c] 1% Au/C catalyst; reaction time, 1 h.

[d] Particle diameters of the supported Au/C catalyst determined by XRPD.

is probably the cause of the different mean diameter values obtained by XRPD in the different preparations immobilized on carbon. These heterogeneous catalysts were used in the oxidation of ethylene glycol and showed low conversions (TOF = 130–300; Table 2), in accordance with supported particle diameters of 9 to 15 nm. As for polydispersion, any comment on a possible relation between TOF and mean diameter is redundant. Based on former work (18) the large particles obtained discouraged us from testing the present sol for immobilization on TiO₂.

Au(0)/SnCl₂/PVA System

NaAuCl₄ is recognized as being the best precursor in this system, highlighting the effect of charges in the stability of this sol. In particular, two different colloids (A and B) were tested on C and TiO₂ supports (Tables 3 and 4). Light-brown sols (A) were obtained at room temperature, reducing both AuCl₃ and NaAuCl₄ at low PVA and Sn(II)/Au ratios (PVA/Au = 0.3 and Sn(II)/Au = 3; Table 3). The colloidal nanoparticles, with a mean diameter close to 4.0 nm

TABLE 3

Au(III)/Sn(II)/PVA System and Heterogeneous Catalysts Obtained by Immobilization of the Light-Brown Sols

	[Sol A]	
Precursor	AuCl₃	NaAuCl₄
SnCl₂/Au[a]	3	3
PVA/Au[b]	0.3	0.3
d (nm)[c]	4.1	4.1
TOF Au/C[d]	1360	1720
TOF Au/TiO₂[d]	410	490
d (nm)[e]	9	8

[a] Molar ratio.

[b] Wt/wt ratio.

[c] Mean diameter average of particles determined by TEM of sols.

[d] Reaction time, 0.5 h.

[e] Particle diameters determined by XRPD of the supported Au/C catalysts.

TABLE 4

Au(III)/Sn(II)/PVA System and Heterogeneous Catalysts Obtained by Immobilization of the Red-Brown Sols

	[Sol B]	
Precursor	AuCl₃	NaAuCl₄	HAuCl₄
SnCl₂/Au[a]	10	10	10
PVA/Au[b]	0.65	0.65	0.65
d (nm)[c]	3.0	3.1	3.3
TOF Au/TiO₂[d]	1225	1225	1225
TOF Au/C[d]	n.d.[f]	260	620
d(nm)[e]	n.d.[f]	25	16

[a] Molar ratio.

[b] Wt/wt ratio.

[c] Mean diameters of the particles of sols, determined by TEM.

[d] Reaction time, 1 h.

[e] Particle diameters determined by XRPD of the supported Au/C catalysts.

[f] Not determined.

(TEM), were immobilized on both activated carbon and titania. Only the 1% carbon-supported catalysts showed good conversions, with TOFs between 1360 and 1720 h⁻¹ for Au/C, and between 410 and 490 h⁻¹ for Au/TiO₂ (Table 3). Mean particle size, determined by XRPD for Au/C, revealed a range of 8 to 9 nm. The dimensions of the Au/TiO₂ particles were not detected by XRPD, as the peak of the crystalline titania was superimposed on that of the gold.

Red-brown sols, composed of smaller particles (3.0–3.3 nm, by TEM) were obtained with larger amounts of reducing and protector agents (PVA/Au = 0.65 and Sn(II)/Au = 10; Table 4), it already being known that the amount of reducing agent influences the reduction rate: the higher the amount, the smaller the particles (36). In contrast to the previous sol, the immobilization on titania generated 1% Au catalysts with good activity (starting from AuCl₃, NaAuCl₄, or HAuCl₄, TOF = 1225 h⁻¹), higher than was observed with the light-brown colloids in Table 3. The activity of this sol immobilized on carbon was low (TOF = 260–620 h⁻¹). The mean particle size of the supported particles, as determined by XRPD, was carried out on C with a range of 16 to 25 nm.

Tin was detected in these heterogeneous systems by both XPS and ICP analyses (about 1%, an amount comparable to that of Au) and its effect on the reactivity was considered. Blank experiments, carried out in the absence of gold (but in the presence of a stannous and/or stannic salt), did not show conversion of the substrate in the catalytic test. However, cocatalytic activity, due to Sn(II) or (IV) moieties, cannot be excluded.

We also investigated the effect of PVA/Au on reactivity (Fig. 1). We observed a decrease in the size of the sols with increasing PVA/Au ratio. Supported particles on carbon showed almost the same sizes (24–25 nm, revealed by XRPD). Thus, the activity of these Au/C particles was
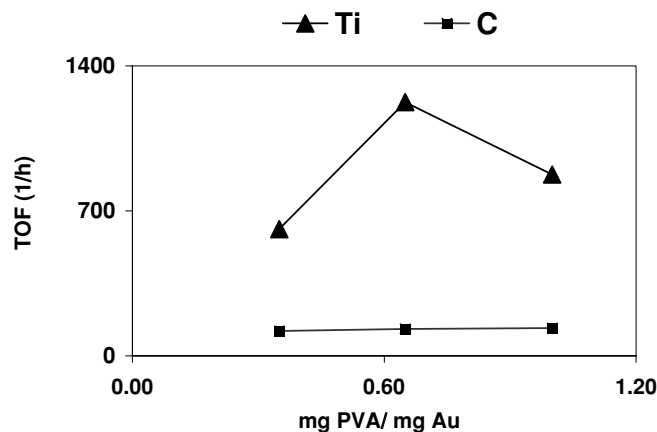
FIG. 1. Role of PVA/Au ratio on reactivity. Comparison of the catalytic activities on C and TiO$_2$. Sol obtained from NaAuCl$_4$ at SnCl$_2$/Au = 10.

also similar, but the maximum activity was found for the Au/TiO$_2$ catalyst derived by the sol with a PVA/Au ratio equal to 0.65. As previous results had showed that the activity of the smaller particles is higher on titania (18), we conclude that we obtained particles of different sizes on the TiO$_2$ support, probably maintaining the same trend in size as was present in the sol.

Au(0)/NaBH$_4$/PDDA System

The cationic polymer poly(diallyldimethylammonium chloride) (PDDA), used in combination with the three gold precursors, proved to be a good stabilizer in colloidal Au(0) synthesis, giving sols composed of particles with a narrow size distribution. Actually, in the sol the absorption of PDDA on the particle increases its surface potential and/or charge density, avoiding coagulation (29).

The reduction of Au(III) compounds was set up in many experimental conditions, varying the NaBH$_4$/Au ratio between 2 and 15; PDDA/Au wt/wt ratios were 0.15 to 1.0. The plasmon peak was detected from UV–vis spectra of the red sols. The wavelength and the molar extinction ($\lambda_{max} = 520$–506 nm; $\varepsilon = 2000$–3000 L mol^{-1} cm^{-1}) were found to be in agreement with TEM micrographs, which had mean diameters of 2.6 to 4.9 nm (26, 36). Table 5 shows the decrease in λ_{max} and particle size with increasing PDDA/Au and NaBH$_4$/Au ratios. In particular, at $\lambda_{max} < 506$ nm the plasmon resonance peak disappears. By combining TEM data and electronic spectra, it was possible to relate the disappearance of the band with a particle size less than 3 nm.

We selected two sols (C and D sols in Tables 6 and 7) on the basis of their small mean diameters and immobilized them on both titania and carbon.

Sol C was generated with small amounts of reducing and protecting agents (NaBH$_4$/Au = 3, PDDA/Au = 0.3). Supported particles generated poor 1% Au/C catalysts, because

the TOF was only about 300 h^{-1} (Table 6). On TiO$_2$ we observed fairly good activity with AuCl$_3$ as the precursor. The activity was substantiated by supported particles of 9 to 13 nm (XRPD measurements).

Sol D was generated with larger amounts of NaBH$_4$ and PDDA and produced smaller crystallites than sol C. TEM analyses showed mean diameters close to 2.7 nm (Table 7).

TABLE 5

NaAuCl$_4$/NaBH$_4$/PDDA System and Variations in λ_{max} with PDDA/Au Ratio

PDDA/Au[a]	NaBH$_4$/Au[b]	λ_{max} UV–vis[c]	d (nm)[d]
0.10	2	520	n.d.[e]
	3	513	5.6
	5	510	4.8
	10	508	3.6
0.15	2	512	n.d.[e]
	3	510	4.3
	5	508	2.7
	10	Undetectable	2.6
0.30	2	n.d.[e]	n.d.[e]
	3	510	4.3
	5	508	2.8
	10	Undetectable	n.d.[e]
0.65	2	508	2.7
	3	508	2.7
	5	506	2.7
	10	Undetectable	2.6

[a] Wt/wt ratio.
[b] Molar ratio.
[c] Nanometers.
[d] Determined by TEM.
[e] Not determined.

TABLE 6

Au(III)/NaBH$_4$/PDDA System and Heterogeneous Catalysts Obtained by Immobilization of Sol C

	[Sol C]		
Precursor	AuCl$_3$	NaAuCl$_4$	HAuCl$_4$
PDDA/Au[a]	0.3	0.3	0.3
NaBH$_4$/Au[b]	3	3	3
d (nm)[c]	3.3	4.3	4.5
TOF (1/h) Au/C[d]	310	320	300
d (nm)[e]	13	9	12
TOF (1/h) Au/TiO$_2$[d]	600	270	n.d.[f]

[a] Wt/wt ratio.
[b] Molar ratio.
[c] Mean diameters of sol particles determined by TEM.
[d] Reaction time, 1 h.
[e] Particle diameters determined by XRPD of the supported Au/C catalysts.
[f] Not determined.

TABLE 7

Au(III)/NaBH₄/PDDA System and Heterogeneous Catalysts Obtained by Immobilization of Sol D

Precursor	[Sol D]		
	AuCl₃	NaAuCl₄	HAuCl₄
PDDA/Au[a]	0.65	0.65	0.65
NaBH₄/Au[b]	10	10	10
d (nm)[c]	2.7	2.6	2.7
TOF (1/h) Au/C[d]	210	140	170
d (nm)[e]	27	22	15
TOF (1/h) Au/TiO₂[f]	1740	2390	1806

[a] Wt/wt ratio.

[b] Molar ratio.

[c] Mean diameters of sol particles determined by TEM.

[d] Reaction time, 1 h.

[e] Particle diameters (determined by XRPD) of supported Au/C catalysts.

[f] Reaction time, 0.5 h.

The immobilization of these colloids on TiO₂ produced quite good heterogeneous catalysts, which exhibited TOF up to 2390 h⁻¹ (Table 7). In contrast, sol D immobilized on carbon showed poor conversion (TOF = 140–210 h⁻¹), in accordance with the large particle sizes detected by XRPD (15–27 nm). We ascribe this big difference in activity to the growth of the particles on carbon.

Figure 2 shows a correlation between particle diameter (in the sol and supported on carbon) and the amount of PPDA for the NaAuCl₄ precursor. It shows that 0.15 is the best PDDA/Au ratio for maintaining the size of sol on carbon. All three gold precursors were reduced in the presence of this amount of PPDA (sol E, NaBH₄/Au = 3; Table 8) and immobilized on activated carbon. Good activity was found, with TOFs from 800 to 880 h⁻¹.

TABLE 8

Au(III)/NaBH₄/PDDA System and Heterogeneous Catalysts Obtained by Immobilization of Sol E

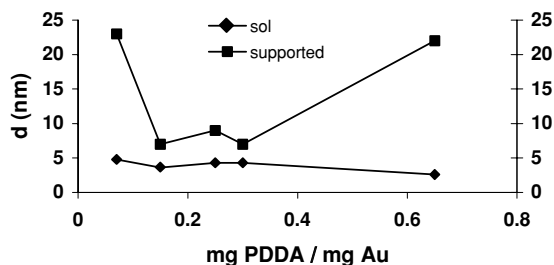| Precursor	[Sol E]		
	AuCl₃	NaAuCl₄	HAuCl₄
PDDA/Au[a]	0.15	0.15	0.15
NaBH₄/Au[b]	3	3	3
d (nm)[c]	3.3	4.3	4.5
TOF (1/h) Au/C[d]	880	840	800
d (nm)[e]	8	7	10

[a] Wt/wt ratio.

[b] Molar ratio.

[c] Sol particle diameters determined by TEM.

[d] Reaction time, 1 h.

[e] Particle diameters determined by XRPD of the supported Au/C catalysts.

FIG. 2. Au(0) particles obtained by NaAuCl₄/NaBH₄/PDDA system: differences between sizes in colloidal solution (TEM) and supported on carbon (XRPD) at different PDDA/Au ratios.

CONCLUSIONS

Many synthetic procedures are known for the production of Au(0) sols, but only a few of them could be used directly as a metallic preformed phase for the production of heterogeneous catalysts (15–19). This is due to the dimensions of the particles (generally active when their size is <10 nm), to the nature of the protective agent (steric or electrostatic influence), and to the dispersing medium (water or solvent). Thus, we conducted experiments to synthesize sol by varying the auric precursors, the reducing agent, and the stabilizing compounds; the aim of the experiments was the production of heterogeneous catalysts to be tested in liquid-phase oxidation.

The nature of the starting gold compounds was not really important, although some enhancements in the final catalytic activity were achieved with NaAuCl₄ (Tables 3 and 7). This enhancement is probably related to the stabilization of the negative gold colloidal particles by sodium counter anions, which enables better dispersion on the supporting material.

The effect of the reducing agent (chemical characteristics and amount) on the dimension and size distribution of the particles was found to be very high. H₂C₂O₄ is not useful for generating good heterogeneous catalysts for liquid-phase oxidation, and SnCl₂ might act as a cocatalyst (Tables 2–4). Thus, NaBH₄ was still the best choice for our experiments, provided that the borate salts (by-products of the reduction) could be removed by washing. As far as the NaBH₄ amount is concerned, we confirmed that the decrease in particle size is due to the increasing molar ratio of the reducing agent to Au (i.e., increasing the rate of the reduction) (Tables 5–8).

Finally, the importance of the protective agent was highlighted. Its influence is well known in sol technology, as the stability of a colloid is a function of the energy of interaction between the particles (23–26). The protective agent stabilizes sol particles against coagulation by electrostatic or steric repulsion (25, 29).

In our present experiments we confirmed the role of the polymer polyvinylalcohol (PVA) in stabilizing gold particles in a catalytic system different from the system

studied previously (17–19). A similar effect was found for the cationic polymeric surfactant poly(diallyldimethylammonium chloride) (PDDA) (Tables 5–8). In this case the stability of the sol was probably accomplished by the formation of an ionic couple with the $AuCl_4^-$ anion (37, 38).

The amount of the protective agent is also important for the immobilization on carbon. On comparing the values in Tables 6 and 8 that differ in PDDA/Au ratios, it can be seen that a lower amount of PDDA produced more active catalysts. The enhancement in activity appeared too high to be explained by the observed decrease in mean size diameter and led us to suspect that other factors (i.e., aggregation, shielding of metallic particle by PDDA) influence activity.

In the case of the PVA-stabilized sol we obtained highly active catalysts when a 0.3 PVA/Au ratio was used (Table 3). With TiO$_2$ as support, we were able to obtain extraordinarily active catalysts (TOF = 1200–2400 h^{-1}; Tables 4 and 7) immobilizing both the PVA and PDDA stabilized gold sols.

In conclusion, let us emphasize the importance of choosing the proper gold sol as a function of support and the reaction for which it is prepared.

ACKNOWLEDGMENT

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