
New Gold Catalysts for Liquid Phase Oxidation

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A pre-requisite for good catalytic activity with supported gold is that the metal is present as nanoparticles, but no suitable method for depositing gold on carbon as nanoparticles has previously been reported. The deposition precipitation method which has been used successfully for catalyst preparation with other supports, produces large aggregates with carbon. It is now shown, however, that pre-reduced gold sol is a satisfactory method for preparing gold on carbon catalysts as long as an appropriate choice of sol is made. In this paper the activity of gold on carbon catalysts prepared in a number of different ways is compared in a standardized liquid phase organic oxidation reaction. The activity for Au/C catalysts prepared by the sol method can show a two-fold increase compared with a similar catalyst prepared by deposition precipitation.

The catalytic activity of both heterogeneous and homogeneous gold based catalysts is now well established in different processes: selective or complete oxidation, hydrochlorination, and hydrogenation reactions (1). All applications show the special reactivity of gold compared with platinum group metals, and this may be explained in terms of the unique electronic state and the high standard electrode potential of gold. Depending on the type of reaction involved, the most active species can be Au(III), as in the case of the hydrochlorination of ethyne (2), or Au(0), as in carbon monoxide oxidation (3), although some doubts have been expressed about the gold oxidation state in the latter reaction when Au/Fe₂O₃ is used as the catalyst (4).

The success of gold as the active metal in catalysis has been mainly due to the development of appropriate methods for depositing gold as nanoparticles (2 – 10 nm) on different supports. The methods most often employed have been co-precipitation, deposition-precipitation and CVD (Chemical Vapour Deposition). Co-precipitation has been used for the preparation of Au/Fe₂O₃ (5), Au/NiO (6), Au/ZnO (7), for use in gas phase carbon monoxide oxidation. It

was shown that gold performance depends on the type of matrix used. Au/ZnO showed the best resistance to deactivation (8), the principal problem to be overcome for their use in practical applications (9). Deposition-precipitation, as well as co-precipitation, is a useful method for supporting gold on oxidic supports such as TiO₂, MgO and Al₂O₃ (10).

It is clear from recent work on the characterization of gold on alumina (11), that addition of base to the chloroauric solution creates six kinds of major species, of which only one [Au(OH)₃] precipitates. As a result, the gold is only partially deposited on the support before the reduction step. Thus, this method has to be strictly controlled in terms of both initial pH value and reduction time, the resulting dimension of the gold particles being dependent on these two parameters, as outlined in the case of Mg(OH)₂ (12). The smallest supported gold particles (<1 nm) reported to date were generated by this method on Mg(OH)₂ (12), where it was observed that a relationship exists between the structure of gold particles and their activity in carbon monoxide oxidation. On the basis of the DFA (Debye Function Analysis) data, icosahedral structures of gold were found to be more active than cubic.

Deposition-precipitation is unfortunately not applicable in the presence of supports such as SiO₂, which have a point zero charge (PZC) at a low pH (about 2 for SiO₂). Thus, for such a material, the deposition of gold by CVD (Chemical Vapour Deposition) has been used, involving the decomposition of a volatile organic compound to gold metal (typically (CH₃)₂Au(acac) where acac = CH₃COCH₂COCH₃) (13). In a comparative study on the activity of gold deposited by the CVD technique on different oxide supports (Al₂O₃, TiO₂ and SiO₂) for gas phase carbon monoxide oxidation at 273K, it was revealed that the nature of the support is not a governing factor in determining the catalyst activity when gold is deposited on a support having a strong interaction with the metal (14). This important conclusion was limited to the particular reaction (carbon monoxide oxidation) and the particular experimental conditions, the support effect being more evident when the gold on oxide catalysts were prepared by the deposition-precipitation method (10a, 15).

A procedure similar to CVD was recently used to prepare gold catalysts on TiO₂ support, and maximum activity for carbon monoxide oxidation was observed for 3.2 nm gold particles evaluated in the 2.5 – 6 nm range, indicating the structure-sensitive nature of the catalysts for gas phase carbon monoxide oxidation (16).

Silicate embedded gold particles are hardly ever used as oxidation catalysts – they are mostly used for analytical purposes; such materials are prepared using a sol-gel method (17). This methodology produces mean particle sizes in the 5 – 6 nm range, involving materials derived from soluble precursors which form a three dimensional network on adding base. However, a typical support used for liquid phase oxidation such as carbon is, in principle, excluded from sol-gel as well as from co-precipitation preparations.

On the contrary, the impregnation technique is of general application and its use has recently been reported for gold using phosphine complexes (18). In this context, for iron oxide supported catalysts, particular attention was paid to the influence of textural properties of the support on both gold particle size and activity in carbon monoxide oxidation, and small gold particles (2.9 nm mean diameter) on poorly crystallized iron oxide (α , γ) were found to be the most active catalyst (18c).

In principle, also the recently reported preparation method involving 'size-socontrolled' colloids is of general application (19). Oxide supports, such as TiO₂ and ZrO₂, have been shown to be suitable adsorbing agents for nanometer scale gold sol generated by reduction of HAuCl₄ with partially hydrolysed

tetrakis(hydroxymethyl)phosphonium chloride (THPC).

As briefly summarized above, most studies on gold catalysts have been focused on gold on oxide supports as these catalytic systems are mostly used for gas-phase oxidation. However, as recently reported, gold catalysts also represent a useful alternative to platinum group metals systems for liquid phase oxidation (20). In this case, the presence of a solvent such as water dramatically affects the interaction between the reagent and the catalytically active materials. In particular, gold on carbon shows superior selectivity and is much less affected by poisoning, when compared with classical palladium and platinum catalysts. As poisoning represents one of the major drawbacks limiting industrial application of liquid phase oxidation involving oxygen as the oxidant, the advantage of using a gold catalyst may not be of only academic interest but could also have industrial potential. As a consequence, there is a growing need for a general procedure to prepare gold catalysts with high dispersion, regardless of the support used.

METHODS FOR PREPARING CARBON SUPPORTED GOLD CATALYST

As recently reported, carbon appears to be the most suitable support for liquid-phase oxidation of diols. In fact, gold on carbon shows better catalytic activity than gold on alumina (20b) and other oxide materials such as silica or Fe₂O₃ (20a), and also better selectivity for glycolate production from ethane-1,2-diol (ethylene glycol) and, more generally, towards the primary alcoholic function with respect to the secondary one. Consequently, we have focused our attention on the optimization of the gold-on-carbon preparation. As in the past we have used classical methods such as impregnation or deposition-precipitation, our approach was firstly to fully investigate the differences between the catalysts prepared by these two techniques; and secondly to study a new method for preparing gold catalysts. As a reference catalytic test we adopted the liquid phase oxidation of ethane-1,2-diol under standard conditions (pO₂ = 2 atm, diol/Au ratio = 1000, diol/NaOH ratio = 1, T = 70°C, reaction time = 1h).

Pore-Volume Impregnation and Deposition-Precipitation Catalysts

The procedures for these techniques have already been reported (20). Activated carbon from Chemviron (AS 800-900 m² g⁻¹, pore volume 0.6 ml g⁻¹, pH 9-10) was used without pre-treatment in all experiments. Table 1

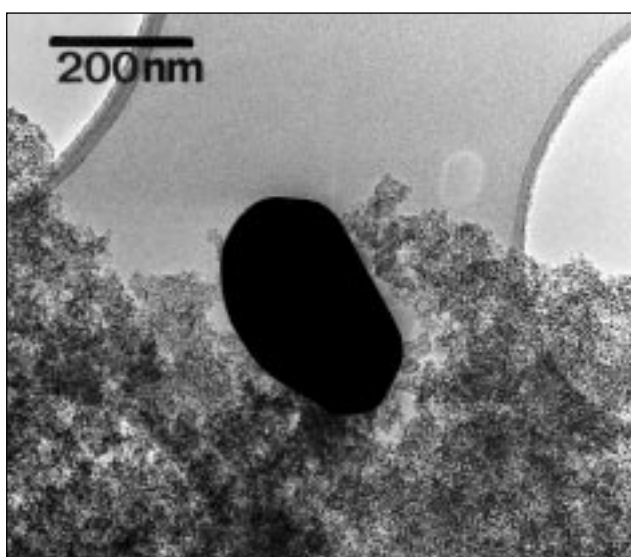
Table 1 Oxidation of Ethane-1,2-Diol using 1%Au/C Catalysts Prepared by a Classical Route⁰

Entry	Catalyst Preparation ^a	Mean Size (nm)		Catalyst Test ^b	
		HRTEM	XRPD	Conversion (mol%)	Selectivity (%) to GLY ^c
1	PVI	350	15.8	22	>99
2	DP A (pH 8)	21	9.8	35	97
3	DP A (pH 10)	13	8.4	43	>99
4	DP B (pH10)	107	14.3	10	>99

^a PVI: pore volume impregnation; Procedure A: auric solution added to carbon slurry; Procedure B: carbon dipped into auric solution; DP = Deposition Precipitation.

^b Catalytic test: Ethylene glycol (EG) / Au = 1000; EG / NaOH = 1; pO₂ = 2 atm; temperature = 70°C; reaction time = 1h.

^c GLY = sodium glycolate.

**Figure 1** HRTEM image of 1%Au/C prepared by pore volume impregnation.

compares the activities of gold on carbon obtained by pore-volume impregnation and by different precipitation-deposition procedures where the operating pH (8 and 10) and the order of adding the reagents (Procedures A and B) were varied.

The pore-volume impregnation method produces a catalyst with low activity (Table 1, Entry 1), as also did the deposition-precipitation technique when Procedure B was used (Table 1, Entry 4). This latter procedure involves the addition of the support to the Au(III) solution, but we found that a substantial enhancement in catalyst activity could be achieved using reverse addition, *ie* the auric acid solution was added to the carbon slurry (Procedure A) (Table 1, Entry 3), the operative pH value having only a small effect (Table 1, Entries 2 and 3).

The HRTEM (High Resolution Electron Microscopy) images revealed the different nature of

these three catalysts, more so than the XRPD (X-Ray Powder Diffraction) measurements whose data are related to coherently scattering domains (21), whereas the HRTEM data applies to particle dimensions. Figure 1 illustrates a typical gold particle on carbon obtained by pore-volume impregnation, the large particle size (>300 nm) being in good agreement with the low catalytic activity. Figures 2 (a and b) correspond to catalysts obtained by the deposition-precipitation technique but using different procedures (Procedure A in Figure 2a and Procedure B in Figure 2b). With Procedure A a wide distribution of particle size (5-50 nm) forming aggregates is obtained, whereas Procedure B produces jelly-fish shaped gold particles where it is probable that only the external part consists of small gold particles that remain catalytically active.

The different nature of carbon compared to other supports certainly plays a fundamental role in producing these gold aggregates. As we ascribe this behaviour mainly to the reducing nature of carbon (20b) that could limit the gradual and dispersed deposition of Au(OH)₃ on the carbon surface, we turned our attention to supporting previously reduced gold, *ie* metallic sols, in order to obtain a higher dispersion of the gold particles.

Supported Gold Sols

In principle, anchoring metallic sols avoids gold particles aggregating as an organo-shell provides, in solution as well as presumably on the surface, a protection for the single gold particles. However, this shell could interfere with the support as well as with the metallic particles and the reagents, and these interactions must be considered when using these materials as catalysts.

Gold colloids have been known since ancient times, and the attraction of these materials is derived from their colour (ruby-red to blue) and therapeutic properties. More recently, reproducible gold sols have been prepared

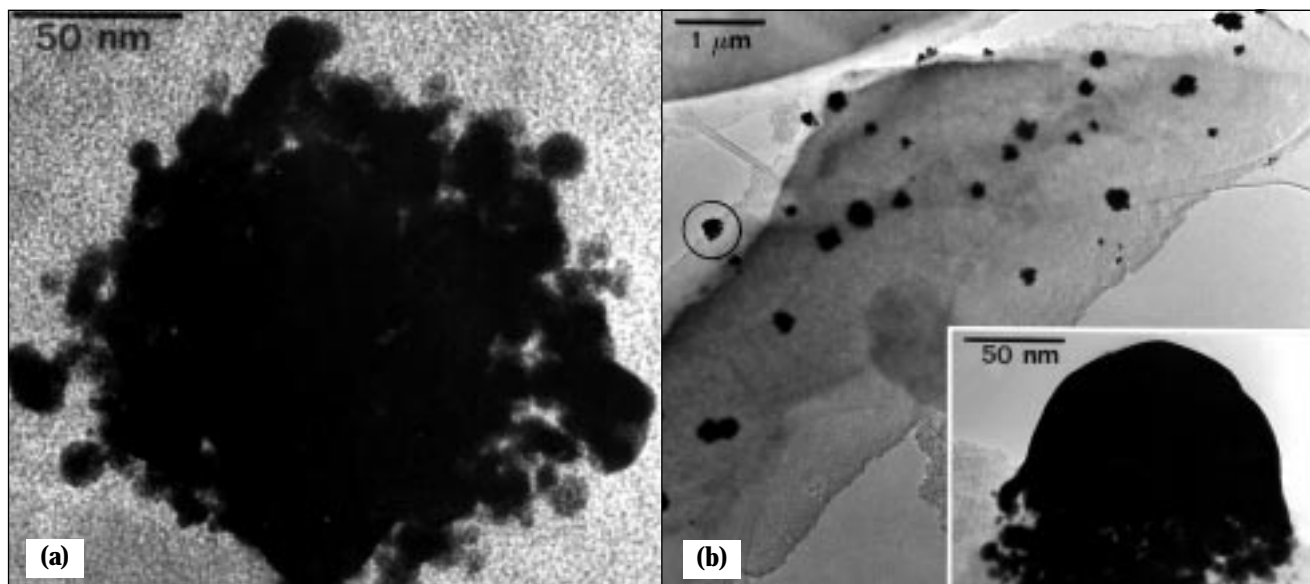


Figure 2 (a) HRTEM image of 1% Au/C prepared by deposition-precipitation (Procedure A)
 (b) HRTEM image of 1% Au/C prepared by deposition-precipitation (Procedure B).

by the reduction of $[\text{AuCl}_4]^-$ with sodium citrate, which also provides an electrical double layer surrounding the gold particles (22). Turkevich's methodology leads to narrow particle size distributions over a range of mean sizes, 10–100 nm, but a standard procedure yields a 20 nm gold sol. There have been many papers describing gold nanoparticle generation and stabilization, even with gold cores containing only 11, 34, 55 gold atoms (23); but as our interest lay in the catalytic properties of gold metal, we focused our attention on preparing gold particles in a diameter range of 1–10 nm where the metallic character should be preserved and the specific catalytic properties of gold should be observed (15). Thus, as a preliminary approach, we focused our attention on the classical generation of protected sols involving the reduction of Au(III) salts in the presence of the macromolecules poly(vinyl pyrrolidone) (PVP) (24) or poly(vinyl alcohol) (PVA) (25).

The first method involving the reduction of NaAuCl_4 by methanol at reflux (80°C) in the presence of PVP had two principal limitations: the amount of PVP required to prevent the aggregation of gold particles was very high (PVP/Au = 6 wt/wt); even in the presence of large quantities of PVP the mean dimension of the gold particles was not less than 8 nm but appeared to be quite independent of the PVP/Au ratio (Table 2). In addition, probably as a result of the large amount of PVP present, active carbon does not adsorb these sols. Thus the solvent must be evaporated, and the by-products of the reduction process and eventually the excess of PVP are also adsorbed. Moreover, as indicated in Table 2, the catalytic activity of comparable gold particles decreases on increasing the amount of PVP, providing evidence for the inhibiting effect of the PVP molecule on the catalytic activity.

By using room temperature reduction in the presence of PVA (25), we had more success both in controlling the

Table 2 Oxidation of Ethane-1,2-Diol using 1% Au/C from PVP-Protected Gold Sol

PVP(mg/ml)	PVP/Au(mg/mg)	d (nm) of Gold Particles		Conversion(%)
		Solution (HRTEM)	Supported in (XRPD)	Catalytic Test ^a
4.8	24	7	8	0
2.5	12.5	8	7.6	18
1.2	6.4	8	8.7	23

^a Catalytic test: Ethylene glycol (EG) / Au = 1000; EG / NaOH = 1; $p\text{O}_2 = 2$ atm; temperature = 70°C, reaction time = 1h; $\text{NaAuCl}_4 = 10^{-3}$ M

Table 3 Oxidation of Ethane-1,2-Diol using 1%Au/C from PVA-Protected Gold Sol.

Entry	HAuCl ₄ (ug/ml) ^a	Mean Size (nm)		Catalyst Test ^b	
		HRTEM	XRPD	Conversion (mol%)	Selectivity (%) to GLY ^c
1	50	4.7	5.5	80	87
2	100	7.5	8	100	96
3	150	21	33	21	78
4	100 ^d	n.d.	6	78	92

^a PVA / Au (wt / wt) = 0.62; NaBH₄ / Au (mol / mol) = 4

^b Catalytic test: Ethylene glycol (EG) / Au = 1000; EG / NaOH = 1; pO₂ = 2 atm; temperature = 70°C; reaction time = 1 h.

^c GLY = sodium glycolate

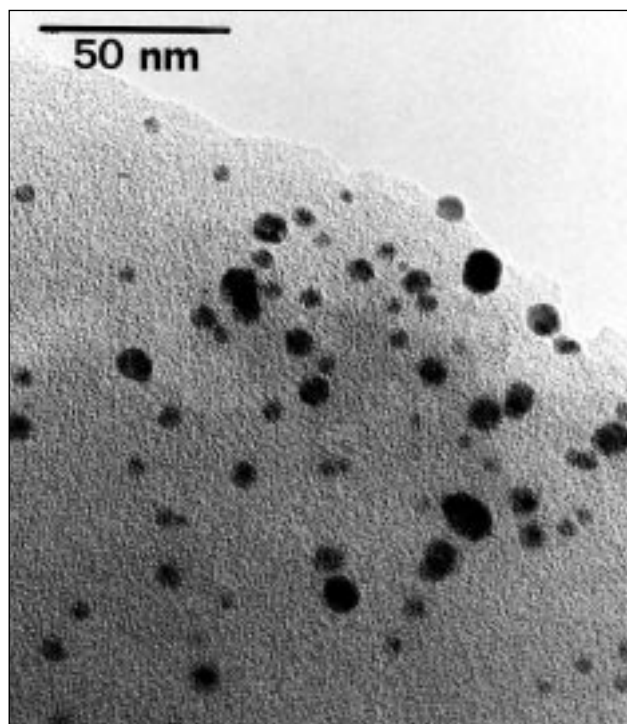
^d PVA / Au (wt / wt) = 1

particle size distribution and having gold sols easily and quantitatively adsorbed by simply adding the carbon. Scipio reported (25) that by varying the initial HAuCl₄ concentration from 6 to 110 μg ml⁻¹ it is possible to obtain, after NaBH₄ reduction, gold particles with a mean diameter of 1.8 – 5.5 nm. Since from a preparative point of view a large volume of solution is a disadvantage, we chose to use an HAuCl₄ solution as concentrated as possible, fixing the PVA/Au ratio at 0.62 (wt/wt) and NaBH₄/Au at 4 (mol/mol) to ensure the complete reduction of Au(III) to Au(0). In line with the prediction, by diluting the gold solution from 150 to 100 to 50 μg ml⁻¹ we obtained smaller particles, the typical λ attributed to gold surface plasmon extinction shifting to lower frequencies (540 to 528 to 512 nm) (26). The mean diameter of the gold particles obtained in the supported samples was in good agreement with UV-Vis sol spectra. Note that in these cases the HRTEM and XRPD measurements give very similar values of mean size, indicating a low crystallographic disorder of the particles (Table 3). From a catalytic point of view, two significant observations can be made:

- by using metallic sols as precursors, a good dispersion of gold particles can be obtained on carbon (Figure 3), greatly enhancing the catalytic activity of this catalyst in the liquid phase oxidation of ethane-1,2-diol (ethylene glycol) (Table 3, Entry 2).
- maximum activity and selectivity is obtained with particles having a mean size of 7-8 nm, with larger and smaller particle sizes being less active and less selective (Table 3, Entries 1, 2 and 3).

Considering the latter point, we carried out some experiments in order to elucidate the possible role of the protective shell. Using a gold concentration of 100 μg ml⁻¹ and a PVA/Au ratio of 1 (wt/wt), we obtained

supported gold particles that XRPD analysis showed to be similar in size to that obtained using a lower gold concentration (50 μg ml⁻¹) and a lower PVA/Au ratio (0.62 wt/wt) (Table 3, entries 1 and 4). As these two catalysts gave almost the same activity (78 and 80% conversion respectively), we concluded that the influence of the PVA molecule in catalysis is negligible. This conclusion is also supported by the fact that adsorbing a PVA solution on a pre-formed catalyst produced no variation in catalytic performance.

**Figure 3** HRTEM image of 1%Au/C prepared by absorption of PVA-protected gold sol.

CONCLUSIONS

Gold on carbon has been found to be a good catalyst for selective liquid phase oxidation of ethane-1,2-diol. The advantage of using gold catalysts lies in its high resistance to poisoning, which is the limiting factor in the scaling-up of liquid phase oxidation using dioxygen. The nature of both the metal (gold) and the support (carbon) makes classical preparation routes unsuitable for obtaining well-dispersed gold particles on carbon. Even deposition-precipitation, the favoured method for preparing highly dispersed gold on oxide supports, failed with carbon, since this gives large aggregates of gold.

Thus, the use of metallic sols as precursors has been demonstrated to be advantageous when preparing gold on carbon catalysts, good dispersion of the gold being obtained as well as enhanced catalyst activity in the liquid phase oxidation of ethane-1,2-diol. It is, however, necessary to choose the appropriate methodology of sol generation and protective molecule in order to achieve a rapid adsorption of sols by carbon and produce a good catalytic material.

In order to optimize the method for preparing gold on carbon catalysts via gold sols, we will extend the reported preparation of gold on oxides employing THPC/NaOH generated gold sol (19) also to carbon. The comparison of the results will be aimed at assessing the influence of the protective molecule in the adsorbing step, in maintaining particle morphology when supported on different materials, and its role in liquid phase oxidation.

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REFERENCES

- 1 D. Thompson, *Gold Bull.*, 1998, **31**, 111 and references cited therein
- 2 B. Nkosi, N.J. Coville, G.J. Hutchings, M.D. Adams, J. Friedl, and F. Wagner, *J. Catal.*, 1991, **128**, 366
- 3 See for example: M. Okumura, N. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, *Catal. Lett.*, 1998, **51**, 53 and references cited therein
- 4 F.E. Wagner, S. Galvagno, C. Milone, A.M. Visco, L. Stievano and S. Calogero, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 3403
- 5 M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, **115**, 301
- 6 W.-X. Zhang, Y.-G. Tao, M.-J. Ming, T.-H. Wu and X.-M. Li, *Gaodeng Xuexiao Huaxue Xuebao*, 1998, **19**, 1317; CA, 129: 180615 (1998)
- 7 G.J. Hutchings, *Gold Bull.*, 1996, **29**, 123
- 8 G.J. Hutchings, M.R.H. Siddiqui, A. Burrows, C.J. Kieley and R. Whyman, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 187
- 9 G. Srinivas, J. Wright, C.-S. Bai and R. Cook, *Stud. Surf. Sci. Catal.*, 1996, **101**, 427
- 10a M. Haruta, *Catalysis Surveys of Japan*, 1997, **1**, 61
- b S. Tsubota, D.A.H. Cunningham, Y. Bando and M. Haruta in 'Preparation of Catalysts VI', ed. G. Poncelet, J. Martens, B. Delmon, P.A. Jacobs and P. Grange Vol. 91, p.227, Elsevier, Amsterdam, 1995
- 11 C.-K. Chang, Y.-J. Chen and C.-T. Yeh, *Appl. Cat. A: General*, 1998, **174**, 13
- 12 D.A.H. Cunningham, W. Vogel, H. Kageyama, S. Tsubota and M. Haruta, *J. Catal.*, 1998, **177**, 1
- 13 M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura and M. Haruta, *Stud. Surf. Sci. Catal.*, 1998, **118**, 277
- 14 M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, *Catal. Lett.*, 1998, **51**, 53
- 15 M. Haruta, *Catal. Today*, 1997, **36**, 153
- 16 M. Valden, S. Pak, X. Lai and D.W. Goodman, *Catal. Lett.*, 1998, **56**, 7
- 17a S. Barathi and O. Lev, *Anal. Commun.*, 1998, **35**, 29
- b S. Barathi and O. Lev, *Chem. Commun.*, 1997, 2303
- c H. Yanagi, S. Mashiko, L.A. Nagahara, H. Tokumoto, *Chem. Mater.*, 1998, **10**, 1258
- 18a Y. Yuan, K. Asakura, H. Wan, K. Tsai, Y. Iwasawa, *Chem. Lett.*, 1996, 755
- b Y. Yuan, A.P. Kozlova, K. Asakura, H. Wan, K. Tsai, Y. Iwasawa, *J. Catal.*, 1997, **170**, 191
- c A.P. Kozlova, S. Sugiyama, A.I. Kozlov, K. Asakura, Y. Iwasawa, *J. Catal.*, 1998, **176**, 426
- 19 J.-D. Grunwaldt, C. Keiner, C. Wögerbauer and A. Baiker, *J. Catal.*, 1999, **181**, 223
- 20a L. Prati and M. Rossi, *Stud. Surf. Sci. Catal.*, 1997, **110**, 509
- b L. Prati and M. Rossi, *J. Catal.*, 1998, **176**, 552
- 21 D.M.A. Guerin and A.G. Alvarez, *Cryst. Rev.*, 1995, **4**, 261
- 22a J. Turkevich, P.C. Stevenson and J. Hillier, *Disc. Faraday Soc.*, 1951, **11**, 55
- b J. Turkevich, *Gold Bull.*, 1985, **18**, 86
- 23a P.A. Bartlett, B. Baure and S.J. Singer, *J. Am. Chem. Soc.*, 1978, **100**, 5085
- b B.K. Teo, X. Shi and H. Zhang, *J. Am. Chem. Soc.*, 1992, **114**, 2743
- c G. Schmid, *Chem. Rev.*, 1992, **92**, 1709
- 24 H. Hirau, Y. Nakao and N. Toshima, *J. Macromol. Sci. Chem.*, 1979, **A13**, 727
- 25 R.G. Scipio, *Anal. Biochem.*, 1996, **236**, 168
- 26 U. Kreibitz and L. Genzel, *Surf. Sci.*, 1985, **156**, 678