Preparation of nanometeric gold particles on NaHY

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Two Au/NaHY systems examined by TEM were prepared using an autoreduction method of Au^{3+} by its ethylene diamine ligands. When about 10% of the cations are H^+ the particle diameter distribution is found to be about 2 nm and homogeneous. If 75% of cations are H^+ the gold particle distribution is centered around 3–4 nm. Gold particles are of good stability when exposed to H_2 at 573 K for two days and the stability under O_2 greater with the higher acidified zeolite.

Keywords: gold particles; zeolite; TEM

1. Introduction

Many authors have shown that supported monometallic gold is surprisingly active compared to bulk gold, which is inert. Under certain conditions it catalyses both dioxygen [1–3] and dihydrogen [4,5] transfer reactions, as well as isomerisation [6]. However, irrespective of the support used and the particle size obtained, gold shows for all these reactions lower activity than group VIII metals. This fact is attributed to the absence of unpaired d electrons in the electronic structure of gold ($[Xe]4f^{14}5d^{10}6s^1$), which results in an inability to chemisorb dioxygen and dihydrogen at ambient temperature. On the other hand, supported gold can be very selective, sometimes more than other metals; this is the case, for example, in the hydrogenation of pent-1-ene to pentane [4] or the oxidation of pentan-1-ol to pentanal by NO_2 [7].

Another interesting aspect of the use of gold in heterogeneous catalysis is in the preparation of supported bimetallic catalysts where it is associated with group VIII metals, notably Pd [8,9] and Pt [10,11]. The gold is introduced either with a view to increasing the dispersion of the more active metal, or to increase the turnover number, its selectivity or its stability. Catalytic tests performed on bimetallic systems based on gold have sometimes confirmed its effect on the activity and the selectivity of the other metal [11,12].

The various preparations of monometallic systems, Au/SiO_2, Au/MgO and Au/Al_2O_3, have demonstrated that it is difficult to obtain small monodispersed gold particles [4,5,13,14]. The particles obtained have an average diameter between 3 and 100 nm on SiO_2 and MgO and between 3 and 220 nm on Al_2O_3 depending on the method of preparation. The tendency of gold to agglomerate in relatively large metallic aggregates appears to be related to its low melting and Tammann temperatures [15]. To limit the growth of gold particles, less traditional supports have been used, sometimes successfully, as with ZrO_2 [16] and TiO_2 [17,18]. On this latter, Haruta [19] obtained particles about 2 nm in diameter by precipitation–deposition, and he also developed a method of preparation by coprecipitation of $HAuCl_4$ and transition metal oxides leading also to ultra-dispersed, thermally stable particles [3]. The catalysts obtained by these two methods are very active in the oxidation of CO at low temperature. To explain these results the authors conclude that there is a strong metal–support interaction, but they were unable to choose between an interaction of a physical or a chemical type.

This work is devoted to Y zeolite, a relatively uncommon support for metallic gold. Zeolites are often employed to disperse the most active transition metal catalysts. The first work concerning gold supported on a zeolite was reported by Boudart [20]. The size of the gold particles obtained by photochemical reduction in NaY faujasite is compatible with their being located inside the zeolite lattice. These clusters are relatively unstable thermally; their size increases with the treatment temperature. Boudart assumed that this effect was due to migration of the particles outside the zeolite crystallites, and Fraissard [21] confirmed this by ^{129}Xe NMR.

We have attempted to prepare small monodispersed and thermally stable gold particles in a NaY zeolite. The samples were prepared by an original method in which the metallic precursor and the support play an important part in the formation of the gold particles. It turned out that the use of partially acidified zeolites $Na_{(1-x)}H_xY$ favours the dispersion of the gold.

2. Experimental

2.1. Preparation

The well known method [22] of preparation by cation exchange, calcination in dioxygen and reduction by dihydrogen at high temperature gives good results for the dispersion of Pt, Rh, Ir and Pd. It fails when one tries to introduce gold onto this support since the particles obtained are not smaller than 10 nm and can appear in the form of aggregates, some of which reach several tens of micrometers. These particles therefore are mainly outside the zeolite lattice.

A method was therefore developed to disperse the gold more efficiently. From industrial faujasite (LZY-54) from UOP (NaY, Si/Al = 2.70) two supports of general formula $Na_{(1-x)}H_xY$ were prepared by exchange in solution of the compensation Na^+ cations by NH_4^+. The exchanged zeolites are dried were then treated in an inert atmosphere for 30 h with a slow rise in temperature (temperature gradient: 12 K/h) up to 673 K and then held at this temperature for 10 h. In this way one obtains $N_{0.9}H_{0.1}Y$ and $Na_{0.25}H_{0.75}Y$ by exchanging 10 and 75%, respectively, of the Na^+ ions (experimental values: 10.9 and 75.8%). The gold is then introduced by ion exchange from the $[Au(en)_2]^{3+}$ complex (en: ethylene diamine) whose synthesis is described by Block and Bailar [23]. After solution of an appropriate amount of the $[Au(en)_2]Cl_3$ in 125 ml of water, 2 g of the modified zeolite were added so as to introduce 0.06 mmol of gold per gram of zeolite (~ 1.3% by weight after reduction). The mixture is stirred for 24 h at 333 K, filtered and washed thoroughly with distilled water to eliminate chlorides. After drying at room temperature for 12 h, the samples are heated in an inert atmosphere (argon : flow rate 6 ℓ/h) in a glass reactor. The reduction of Au^{3+} by its ligands is realised by raising the temperature linearly in 2 h from room temperature to 423 K, then held at this temperature for 4 h. After cooling in argon the samples obtained are mauve.

In order to study the stability of the gold particles, each sample is thermally treated for 48 h in dioxygen or dihydrogen (flow rate: 1.5 ℓ/h) at 573 K. The nomenclature and the weight percentage of gold, determined by elemental chemical analysis, are given in table 1.

2.2. *Transmission electron microscopy (TEM)*

The samples were examined on a JEM 100 CX II (Jeol) microscopic resolution 0.3 nm. TEM after reduction and after prolonged thermal treatment in dihydrogen or dioxygen. The direct image, magnified 465 600 times, of the supported metallic particles is used to determine the size distribution and the corresponding mean diameter. To draw the histograms 350 to 1000 particles have to be counted on several micrographs per sample. Most of the samples were sectioned in order to check that the metal was inside the zeolite lattice.

3. Results and discussion

3.1. *Chemical analysis and "autoreduction" method*

Chemical analyses performed on the two series of samples reveal the presence of carbon (~ 0.3 wt%) and nitrogen (~ 0.6 wt%). Comparison with results on a $Na_{0.25}H_{0.75}Y$ zeolite not exchanged with $[Au(en)_2]^{3+}$ (C: 0.04 wt%, N: < 0.3 wt%) suggests that these elements arise from the ethylene diamine ligands used to reduce the cations. Carbon and nitrogen analyses on samples heated under dioxygen indicate that this treatment leads to the elimination of 75% of the nitrogen and 60% of the carbon.

The weight percentages, determined by chemical analysis, indicate that exchange between the $[Au(en)_2]^{3+}$ complex in solution and the compensating cations of the zeolites is complete (table 1). In order to avoid fritting the gold, the preparation of the particles in the zeolites does not follow the calination (O_2)/reduction (H_2) procedure usually employed for this type of support. When samples containing Pt, Pd, Rh, etc. are prepared there is usually a calcination step (under dioxygen or air, most often at 573 K) in order to decomplex the metal cations and avoid their reduction by the ligands, which leads to a poor dispersion of the metal [24]. It is during this step that the "bare" cations migrate from the supercages, where they are introduced in the exchange, towards the sodalite cages where they are better coordinated and where they are reduced to form small particles. As for gold, we have observed that the Au^{3+} cation is reduced to Au^0 by its ethylene diamine ligands even at 343 K; calcination is therefore impossible. This temperature should not be exceeded even during the exchange in solution, failing which premature reduction occurs. It is this carefully controlled process of "autoreduction" which is used for the preparation of metallic particles. The complexed cation is reduced in an inert atmosphere (argon) at a temperature low enough to avoid the migration of

Table 1
Name and metal content of samples

Name	Support	Treatment after reduction	Au loading nominal (wt%)	Au loading exptl (wt%)
F	$Au/Na_{0.9}H_{0.1}Y$	–	1.24	1.07
F1	$Au/Na_{0.9}H_{0.1}Y$	O_2, 573 K, 48 h	1.24	1.16
F2	$Au/Na_{0.9}H_{0.1}Y$	H_2, 573 K, 48 h	1.24	1.12
G	$Au/Na_{0.25}H_{0.75}Y$	–	1.30	1.16
G1	$Au/Na_{0.25}H_{0.75}Y$	O_2, 573 K, 48 h	1.30	1.19
G2	$Au/Na_{0.25}H_{0.75}Y$	H_2, 573 K, 48 h	1.30	1.24

the metal outside the zeolite crystallites but high enough (423 K) to allow complete reduction of the ions. Since the critical step of decomplexation is not achieved, one can assume that the gold particles formed are exclusively in the supercages. A recent study on the Ru/NaY system shows that the autoreduction of the $[Ru(NH_3)_6]^{3+}$ complex under argon leads to particles of about 1 nm only in the faujasite supercages [25].

The mauve colour of the samples after reduction, previously observed by others, is the characteristic colour of gold in a colloidal state. Galvagno [5] states that the colour of reduced gold depends mainly on the size of the particles and their distribution, on the amount of gold introduced into the support, but also on a possible metal–support interaction. For particles with a mean diameter of 3 nm the colour is pale blue on MgO, violet on Al_2O_3 and mauve on SiO_2. Since the frequency of the visible transition responsible for the colour of gold is related to the energy of the 5d electrons, Galvagno suggests that the support is responsible for the colour variation and that it modifies the electronic energy levels. A chemical interaction increasing in the order: $MgO < Al_2O_3 < SiO_2$ would explain the increase in the frequency of the optical transition of metallic gold on these supports. Following this model, for 3 nm particles the Au/NaHY system would involve a metal–support interaction of the same order of magnitude as the Au/SiO_2 system.

3.2. *Transmission electron microscopy (TEM)*

TEM of sections shows that the dispersion of the gold is good and that the distribution of the particle size in $Na_{(1-x)}H_xY$ zeolites after reduction (samples F and G) is homogeneous. In figs. 1 and 2 are presented the particle size distributions (percentage of particles against size class) for Au/$Na_{0.9}H_{0.1}Y$ (F, F1 and F2) and Au/$Na_{0.25}H_{0.75}Y$ (G, G1 and G2). The mean diameters, defined by: $d_{TEM} = \sum nidi / \sum ni$, were calculated from the size histograms (see table 2). These show a difference between the particle size distribution for samples F and G, for which the acid content of the support is different ($Na_{0.9}H_{0.1}Y$ and $Na_{0.25}H_{0.75}Y$, respectively). In sample F the particles are distributed more homogeneously around 2 nm, which gives a mean diameter of 2.8 nm, less than that of G (3.4 nm). Reproducibility tests confirmed this difference between the two zeolites.

Figs. 1a and 1c compare samples which have been freshly reduced (F) and treated with dihydrogen (F2) on the less acidic zeolite. The distribution profiles are similar, with 70% of the particles in the 1–3 nm range, and the mean diameter is constant during the thermal treatment. On the more acidic zeolite (G and G2) the particles are similarly distributed (figs. 2a and 2c): 80% of them lie in the 1–5 nm range (fig. 3). There is a very slight increase in the particle size after treatment in dihydrogen (3.4 to 3.8 nm).

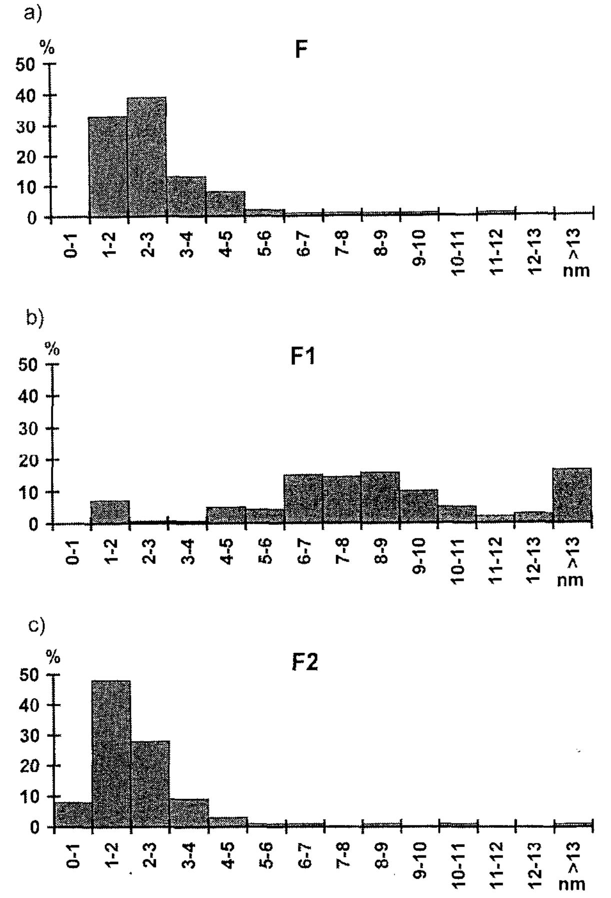

Fig. 1. Particle size histograms for Au/$Na_{0.9}H_{0.1}Y$ samples: (a) freshly reduced (F); (b) after treatment in O_2 at 473 K for 48 h (F1); (c) after treatment in H_2 at 473 K for 48 h (F2).

Thermal treatment in dioxygen affects the particles differently, depending on whether they were prepared on the more or less acidic support. On $Na_{0.25}H_{0.75}Y$ (G1) there is little agglomeration of the metal: the stability of the particles is close to what is observed upon treatment in dihydrogen and most of the particles are in the 3–6 nm range. The good stability of the particles on this support can be seen from fig. 2b. On the other hand, when the Au/$Na_{0.9}H_{0.1}Y$ sample is treated with dioxygen (F1) the distribution is more heterogeneous, the particle sizes ranging from 1 to 16 nm (fig. 1b).

During preliminary work we found it difficult to obtain gold well dispersed on NaY zeolite. Boudart [20,21] had already observed that gold particles, obtained on this support by reduction of $[Au(en)_2]^{3+}$ in dihydrogen, migrate as from 450 K towards the crystallite surfaces, where they agglomerate. The steric constraint of the zeolite, which is usually considered to be the cause of the blockage of particles in the matrix, is therefore not enough in the case of gold. This is explained by the low stability of gold when it is dispersed. The Tammann temperature, at which the metal atoms become mobile, is directly related to the melting point (T_f) [15]. Because its melting point is low ($T_f = 1336$ K) gold has a very low Tammann temperature (445 K).

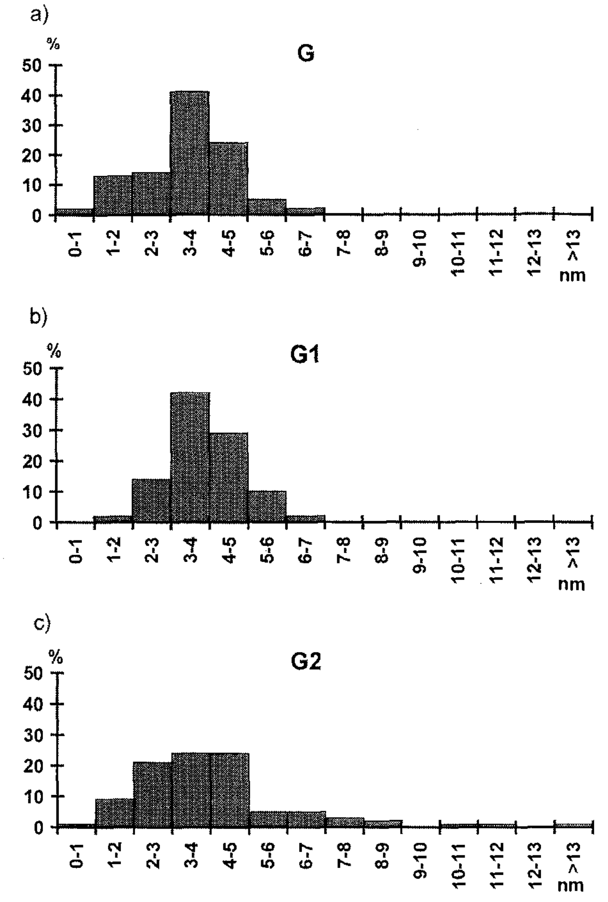

Fig. 2. Particle size histograms for Au/$Na_{0.25}H_{0.75}Y$ samples: (a) freshly reduced (G); (b) after treatment in O_2 at 473 K for 48 h (G1); (c) after treatment in H_2 at 473 K for 48 h (G2).

Moreover, for supported systems this temperature is reduced, metal aggregates having lower melting points than the corresponding bulk metal [26].

The use of Y zeolites where the compensation Na^+ ions have been partially replaced by protons seems therefore to be preferable for the preparation of small metallic gold particles. This observation can be related to the hypothesis of chemical anchorage proposed by Sachtler for faujasite [27]. He suggests that the agglomeration of metal at low temperature can be avoided by anchoring the metal in the zeolite cavity by means of proton bridges ($O \cdots H \cdots M_m$ bonds). This hypothesis is generally accepted for the attachment of small particles of Pt or Pd in faujasite, where it results in the formation of positively charged clusters. Generally, OH groups which are at the origin of these proton bridges are already present in the zeolite or are introduced during the reduction of the metal cation in dihydrogen, the step which generates the protons. In our samples Au^{3+} is reduced by its ligands. When the support is NaY zeolite there are very few protons and there can be no chemical interaction between the support and the gold. The particles obtained grow rapidly, probably in the reduction step (423 K). The situation is different for NaHY where the protons introduced can attach the gold. One can therefore consider that the acidity of the compensating cations is the reason for the good dispersion of gold on the NaHY used.

Table 2
Average diameter of gold particles (nm) in F and G samples

Sample	Support	Average diameter $d_{TEM} = \sum nidi / \sum ni$
F	$Na_{0.9}H_{0.1}Y$	2.8
F1	$Na_{0.9}H_{0.1}Y$	10
F2	$Na_{0.9}H_{0.1}Y$	2.8
G	$Na_{0.25}H_{0.75}Y$	3.4
G1	$Na_{0.25}H_{0.75}Y$	3.9
G2	$Na_{0.25}H_{0.75}Y$	3.8

The difference in the acidity of the zeolites also has an effect on the dimensions of the particles formed. The particles observed in all the samples are mainly greater than 1 nm. Many particles lie between 2 and 5 nm, i.e. larger than the internal diameter of the supercages. Microscopy on sections shows, however, that the gold particles are nevertheless inside the zeolite. Metallic particles (notably Pd, Ru, Pt and Ni) greater than the dimensions of the supercages have often been observed by TEM in the lattice of NaY zeolite [28]. The authors propose that these metal particles grow by a mechanism involving atomic rearrangements of the zeolite lattice, even at temperatures below 600 K. In the case of the growth of Ni on X zeolite [29], the authors advanced this mechanism, suggesting moreover that the protons arising from the reduction of Ni favoured the local destruction of the lattice (probably be weakening the $Si \cdots O$ and $Al \cdots O$ bonds). Such a process would explain that in the more acidic zeolite the supercages are more easily destroyed in the formation of gold particles, and for this reason larger particles are formed than for the freshly prepared sample (sample G).

The histograms obtained after prolonged treatment in dihydrogen at 573 K (F2 and G2) are similar to those of F and G: the particle size and distribution have changed very little. It can be deduced that they would be stable in a chemical reaction where the catalyst was heated in the presence of dihydrogen.

However, the same stability is not observed for particles in dioxygen on $Na_{0.9}H_{0.1}Y$, as is shown by the histogram in fig. 1b and the corresponding mean diameter. The only obvious explanation of this phenomenon is that since there are far fewer OH groups in this zeolite the particles are less efficiently anchored.

4. Conclusion

The method which consists in acidifying NaY zeolite ($Na_{(1-x)}H_xY$) before cation exchange makes it possible to obtain for the first time, by reduction of the ions by ethylene diamine ligands, small gold particles located inside the zeolite lattice. We have therefore a process the performance of which is comparable to that of the meth-

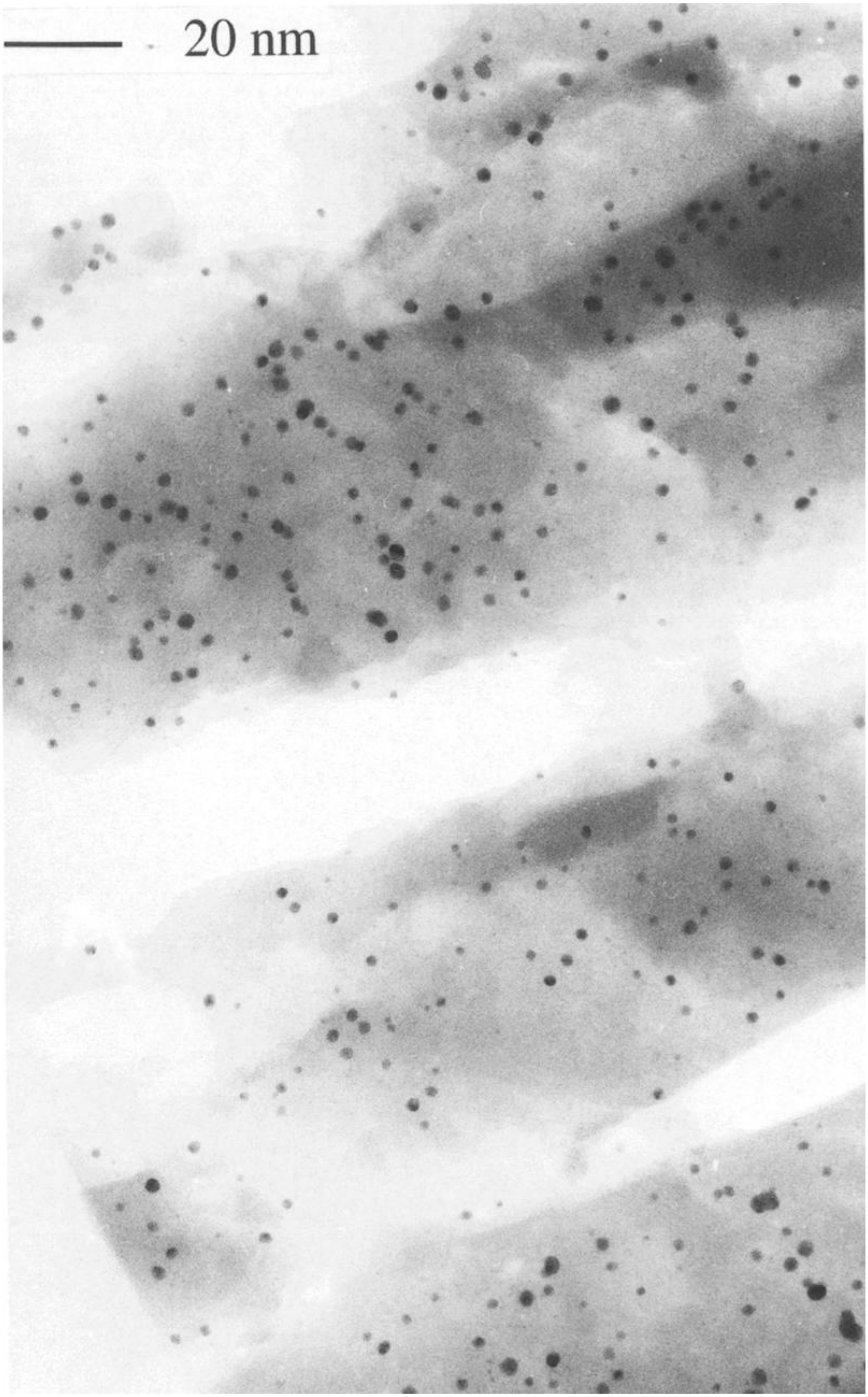

Fig. 3. TEM photograph of $Au/Na_{0.25}H_{0.75}Y$ (sample G), magnification 465 600 times.

ods normally used for the most common catalyst metals (Pt, Pd, etc.) but which cannot be used for gold because of their tendency to cause agglomeration in large clusters outside the zeolite grains.

While the introduction of protons into faujasite allows a good dispersion of gold in the form of particles thermally stable under dihydrogen at high temperature (573 K), only the more acidic faujasite ($Na_{0.25}H_{0.75}Y$) gives particles which are stable in dioxygen at the same temperature.

References

[1] N.W. Cant and W.K. Hall, J. Phys. Chem. 75 (1971) 2914.

[2] W. Linand and M. Flytzani-Stephanopoulos, J. Catal. 153 (1995) 317.

[3] S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda and Y. Nakahama, Stud. Surf. Sci. Catal. 63 (1991) 695.

[4] P.A. Sermon, G.C. Bond and P.B. Wells, J Chem. Soc. Faraday Trans. I 75 (1979) 385.

[5] S. Galvagno and G. Parravano, J. Catal. 55 (1978) 178.

[6] G. Parravano, J. Catal. 24 (1972) 233.

[7] S.A. Nyarady and R.E. Sievers, J. Am. Chem. Soc. 107 (1985) 3726.

[8] R.J. Davis and M. Boudart, J. Phys. Chem. 98 (1994) 5471.

[9] W. Juszczyk, Z. Karpinski, D. Lomot, J. Pielaszek and W. Sobczak, J. Catal. 151 (1995) 67.

[10] V. Bertin, P. Bosch, G. Del Angel, R. Gomez, J. Barbier and P. Maricot, J. Chim. Phys. (Paris) 92 (1995) 120.

[11] D. Rouabah and J. Fraissard, Catal. Lett. 34 (1995) 321.

[12] M.C. Demicheli, L.C. Hoang, J.C. Menezo, J. Barbier and M. Pinabiau-Carlier, Appl. Catal. 97 (1993) L11.

[13] G. Cocco, S. Enzo, G. Fagherozzi, L. Schiffini, I.W. Bassi, G. Vlaic, S. Galvagno and G. Parravano, J. Phys. Chem. 83 (1979) 2527.

[14] S. Lin and M.A. Vannice, Catal. Lett. 10 (1991) 47.

[15] R.T.K. Baker, J. Catal. 78 (1982) 473.

[16] A. Knell, P. Barnickel, A. Baiker and A. Wokaun, J. Catal. 137 (1992) 306.

[17] A.G. Shastri, A.K. Datye and J. Schwank, J. Catal. 87 (1984) 265.

[18] D.G. Duff and A. Baiker, Stud. Surf. Sci. Catal. 91 (1995) 505.

[19] S. Tsubota, D.A.H. Cunningham, Y. Bando and H. Haruta, Stud. Surf. Sci. Catal. 91 (1995) 227.

[20] M. Boudart and G. Meitzner, in: *EXAFS and Near Edge Structure III*, Springer Proceedings 2, eds. K.O. Hodgson, B. Hedman and J.E. Penner-Halm (Springer, Berlin, 1984) p. 217.

[21] J. Fraissard, unpublished.

[22] P. Gallezot, Stud. Surf. Sci. Catal. 83 (1980) 415.

[23] B.P. Block and J.C. Bailar, J. Am. Chem. Soc. 73 (1951) 4722.

[24] D. Exmer, N. Jaeger, K. Moller and G. Schulz-Ekloff, J. Chem. Soc. Faraday Trans. I 78 (1982) 3537.

[25] U. Guntow, F. Rosowski, M. Mulher, G. Ertl and R. Schlögl, Stud. Surf. Sci. Catal. 91 (1995) 217.

[26] J. Ross and R.P. Andres, Surf. Sci. 106 (1981) 11.

[27] W.M.H. Sachtler and A.Yu. Stakheev, Catal. Today 12 (1992) 283.

[28] N.I. Jaeger, P. Ryder and G. Schulz-Ekloff, Stud. Surf. Sci. Catal. 18 (1984) 299.

[29] D. Exmer, N. Jaeger, R. Nowak, H. Schrubbers and G. Schulz-Ekloff, J. Catal. 74 (1982) 188.