Aerobic oxidation of glucose over gold nanoparticles deposited on cellulose

Tamao Ishida [a,c], Hiroto Watanabe [a,c], Takao Bebeko [a], Tomoki Akita [b,c], Masatake Haruta [a,c,*]

[a] Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan
[b] Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan
[c] Japan Science and Technology Agency (JST), CREST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

ABSTRACT

Gold nanoparticles (NPs) with mean diameters of around 2 nm could be deposited directly onto a biopolymer, cellulose, by the solid grinding method with volatile dimethyl Au(III)acetylacetonate followed by the reduction with H_2. Gold NPs on cellulose showed appreciably high catalytic activity with a turnover frequency (TOF) of $11 \, s^{-1}$ for the aerobic oxidation of glucose to produce sodium gluconate at 60 °C and at pH 9.5. The catalytic activity of Au/cellulose was comparable to that of Au/C provided the size of the Au particles was similar.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The catalytic transformation of biomass-derived natural resources into valuable compounds is of great importance for sustainable developments [1]. The aerobic oxidation of glucose to gluconic acid over transition-metal catalysts, including Pd, Pt, and Au, has been extensively studied during the last two decades for applications to food additives and detergents for beverage bottles [2–8]. In particular, Au catalysts have shown higher catalytic activity with excellent selectivity to gluconic acid than Pd and Pt without loading Bi or Pb, as reported by Rossi and his co-workers by using Au on activated carbons (AC) [4]. We have also reported that Au clusters and nanoparticles (NPs) deposited on metal oxides such as Al_2O_3 and ZrO_2 exhibited extremely high catalytic activity for glucose oxidation with a turnover frequency (TOF, reaction rate per surface Au atom) of $45 \, mol_{Glucose} \, mol_{surface \, Au}^{-1} \, s^{-1}$ at 50 °C and at pH 9.0 [8].

Not only metal oxides and carbons but also organic polymers have recently been used as efficient supports to stabilize small Au NPs (2–10 nm in diameter) and clusters (below 2 nm) [9–14]. Biffis et al. investigated the catalytic performance of Au NPs (2.4 nm) supported by polymer gel [12]. These materials showed higher catalytic activity than Au/C for the oxidation of hydrophobic alcohols

such as benzylalcohol but lower activity for glucose oxidation. Therefore, polymer supported Au catalysts which exhibit high catalytic activities in the oxidation of glucose are scarce except for Au NPs supported on strongly basic anion-exchange resin, the metal-time-yield (MTY, reaction rate per total Au atom) of which is $27{,}000 \, mol_{Glucose} \, mol_{Au}^{-1} \, h^{-1}$ ($7.5 \, mol_{Glucose} \, mol_{Au}^{-1} \, s^{-1}$) at 60 °C and at pH 9.5 [13].

On the other hand, we have explored renewable polymeric supports obtained from the natural feedstocks in order to shift to sustainable developments of Au catalysts. Cellulose is the most abundant and easily obtained organic compound in nature, since it is the main component of plants. In addition, cellulose is a promising candidate as a support for metal catalysts owing to the following reasons: (1) chemical stability and resistance to degradation by acids or bases, (2) an oxygen-rich structure as hydroxyl groups that are expected to interact with metal ion precursors and stabilize metal NPs, (3) a hydrophilic nature which seems to be suitable for reactions in aqueous media.

Some researchers exploited cellulose as a support for metal NPs [15–17]. However, the control of nanoparticle properties in terms of shape, size, and stability was difficult on cellulose supports. Kunitake and his co-workers reported that porous cellulose fibers could stabilize small Au NPs with a mean diameter of 3 nm, which were prepared by impregnation method followed by the reduction with $NaBH_4$ [17]. However, the catalytic activity of Au/cellulose has not yet been explored.

Corma et al. prepared Au NPs supported on chitosan-based organic–inorganic hybrid materials and used them as a catalyst for the hydroamination reaction [18]. Although chitosan is also an

abundant natural resource, chitosan by itself cannot be used as a support due to its weak mechanical strength and poor diffusion into solvent.

In this work, in order to establish a generic route to prepare "green" gold catalysts, we have attempted to deposit Au NPs onto cellulose directly from gold complexes by the deposition–reduction (DR) method [19,20] and by the solid grinding (SG) method [14]. We have also studied their catalytic performance for the aerobic oxidation of glucose in aqueous media.

2. Experimental

2.1. Materials

Cellulose (<100 μm powder) was purchased from Aldrich and used as received. Bis(ethylenediamine)gold(III) trichloride ($Au(en)_2Cl_3$) was prepared from $HAuCl_4 \cdot 4H_2O$ according to the literature [21]. Dimethyl gold(III)acetylacetonate, $Me_2Au(acac)$, was purchased from Trichemical Laboratories Inc. and used as received. Reagent grade glucose and NaOH were purchased and used without further purification.

2.2. Instruments

Zeta potentials were measured on a Microtec ZEECOM in 0.01 M NaCl aqueous solution. The pH of the solution was adjusted by adding HCl or NaOH solution. Transmission electron microscopic (TEM) observations were carried out by using a JEOL JEM-3000F operating at 300 kV and a JEM-2100F operating at 200 kV. High-angle annular dark-field scanning TEM (HAADF-STEM) observation was also carried out to observe Au clusters smaller than 2 nm by using a JEOL JEM-3000F. The gold contents of the catalysts were determined by atomic absorption spectrometry (AAS) by using a SHIMADZU AA-6200. The products of glucose oxidation were identified by using ^1H NMR (270 MHz in D_2O) and compared with authentic samples.

2.3. Direct deposition of gold nanoparticles onto cellulose by the deposition–reduction method

To a suspension of cellulose (0.5 g) dispersed in distilled water (100 mL), a solution of $Au(en)_2Cl_3$ (5.4 mg, Au loading 0.5 wt%) in H_2O (5.0 mL) was added. The pH of the suspension was adjusted to 10 by adding aqueous NaOH solution. The mixture was stirred at 0 °C for 30 min and then 0.01 M $NaBH_4$ (1.9 mL) was slowly added over 4 min. After additional stirring at 0 °C for 1 h, the mixture was filtered, washed, and dried under vacuum for 2 h to yield Au/cellulose.

2.4. Direct deposition of gold clusters onto cellulose by the solid grinding method

Cellulose (500 mg) and $Me_2Au(acac)$ (4.2 mg for 0.5 wt% Au loading) were ground in an agate mortar in air at room temperature for 40 min. A small amount of water (0.4 mL) was added during grinding for 40 min. The mixture was treated in a stream of 20 vol% H_2 in N_2 at a flow rate of 50 mL/min at 120 °C for 2 h to reduce Au(III) to Au(0).

2.5. Catalytic tests

Glucose oxidation was carried out at atmospheric pressure by bubbling molecular oxygen (60 mL/min) through the glucose (4.39 g) aqueous solution (74 mL). The catalyst dispersed in H_2O (10 mL) was added into the 5 wt% glucose solution (glucose/loaded Au = 16,000 mol/mol), and the aqueous dispersion was stirred at

60 °C. The reaction was kept at pH 9.5 by titrating 1 M aqueous NaOH solution. The conversion of glucose was calculated from the total amount of NaOH added. Metal-time-yield was calculated from a straight line fitted to the conversion-time curve. Turnover frequency (TOF) was calculated from MTY based on the number of Au atoms exposed to the surfaces, which were calculated from the mean particle diameters.

The rate dependency on glucose concentration was obtained under the following conditions: glucose/Au = 32,000 mol/mol, O_2 120 mL/min, 50 °C, and pH 9.0. The concentration of glucose was changed over the range of 2.5–10 wt%. The rate of glucose oxidation is expressed by Eq. (1) since the flow of O_2 was in large excess with respect to glucose concentration:

$$r = k[\text{glucose}]^a[O_2]^b = k'[\text{glucose}]^a \qquad (k' = k[O_2]^b) \qquad (1)$$

Arrhenius plots were obtained under the following conditions: 5 wt% aqueous glucose solution (glucose/Au = 32,000 mol/mol), O_2 120 mL/min, pH 9.0. The reaction temperature was changed in the range of 40–70 °C.

3. Results

3.1. Direct deposition of gold nanoparticles and clusters onto cellulose

The deposition–reduction (DR) method is based on the use of weak electrostatic interactions of polymer surfaces with the opposite charged Au(III) complex ions, leading to the reduction of Au(III) exclusively on polymer surfaces [19,20]. Cationic $Au(en)_2Cl_3$ was chosen as a Au precursor because of the negative zeta potentials of cellulose in the pH range of 3–10 (Fig. 1). We have reported that the dropwise addition of a reducing agent into an Au(III) aqueous solution was effective to obtain small Au NPs and to prevent them from aggregation [19]. Gold NPs supported on cellulose were also prepared by slow reduction in a similar manner. Most of the loaded Au(III) precursors were reduced to Au(0) exclusively on cellulose surfaces up to 0.5 wt% of Au loading. As shown in Table 1 and Fig. 2, 0.5 wt% of Au loading yielded large Au NPs around 10 nm, accompanied by the formation of aggregates (entry 1, Fig. 2). Lower Au loading (0.05 wt%) gave smaller Au NPs having a mean diameter of 7.7 nm with a standard deviation of 6.0 nm (entry 2).

We have recently reported that the solid grinding method was effective to deposit Au as clusters smaller than 2 nm onto inert supports such as polymers [14], carbons [8,22], and insulating metal oxides [8]. This method was applicable to cellulose and gave highly dispersed Au clusters and NPs with diameters of around 2 nm in the range of 0.05–0.23 wt% of Au content (entries 3–5 in Table 1, Fig. 3). In the case of cellulose, the addition of small amounts of H_2O during grinding was effective to deposit small Au NPs in particular for
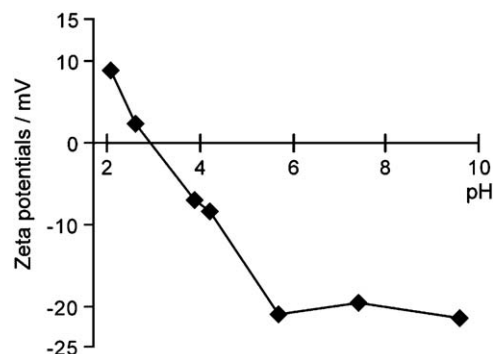

Fig. 1. Zeta potentials of cellulose in 0.01 M NaCl aqueous solution as a function of pH.

Table 1
Preparation of Au/cellulose and their catalytic activity for glucose oxidation.

Entry	Preparation method[a]	Au loading (wt%)	Au content (wt%)[b]	Au particle size (nm)[c]	MTY (h^{-1})[e]	TOF (s^{-1})[e]
1	DR	0.5	0.45	14.5 ± 9.0	6000	–
2	DR	0.05	0.054	7.7 ± 6.0	2000	–
3	SG	0.5	0.23	2.0 ± 1.0[d]	22,000	9.1
4	SG	0.10	0.10	2.5 ± 1.4[d]	21,000	10.6
5	SG	0.05	0.050	2.4 ± 1.9[d]	19,000	9.3

[a] DR: deposition–reduction and SG: solid grinding.
[b] Measured by AAS analysis.
[c] The data were obtained by TEM.
[d] Observed by HAADF-STEM.
[e] Reaction conditions: 5 wt% glucose aqueous solution (84 mL), glucose/Au = 16,000 mol/mol, O_2 60 mL/min, 60 °C. The pH of the solution was kept at 9.5 by titrating 1 M NaOH.

0.5 wt% of Au loading. Although only half of Au could be deposited on cellulose when 0.5 wt% of Au was loaded, the mean diameter did not increase with an increase in Au loading (entry 3).

3.2. Aerobic oxidation of glucose over Au/cellulose

The catalytic performance of Au/cellulose for the aerobic oxidation of glucose is summarized in Table 1. Although the difference in the catalytic activity of Au/cellulose was marginal over 7 nm of Au NPs (entries 1 and 2 in Table 1), the catalytic activity markedly increased once the diameter of Au particles became 2 nm (entries 3–5). The materials exhibited catalytic activity as high as 22,000 h^{-1} (6.1 s^{-1}) in MTY. This value was slightly lower than that of Au/ion-exchange resin (7.5 s^{-1}) [13].

However, Au/cellulose catalysts can be readily obtained by the solid grinding, as compared to ion-exchange resins which require pre-treatment with alkaline solution before the deposition of Au.

Recently, we have reported that small Au NPs were directly deposited onto metal oxides (e.g. Al_2O_3 and ZrO_2) and nanoporous carbon (NPC) at around 2 nm by the solid grinding method [8]. For the glucose oxidation, TOFs were 45 and 2.6 s^{-1} for Au/Al_2O_3 and Au/NPC, respectively. The catalytic performance of Au/cellulose was compared with those of Au/Al_2O_3 and Au/NPC under the same conditions: glucose/Au = 32,000 mol/mol, O_2 120 mL/min, 50 °C, and pH 9.0. As a result, TOF of Au/cellulose was 2.0 s^{-1} which was
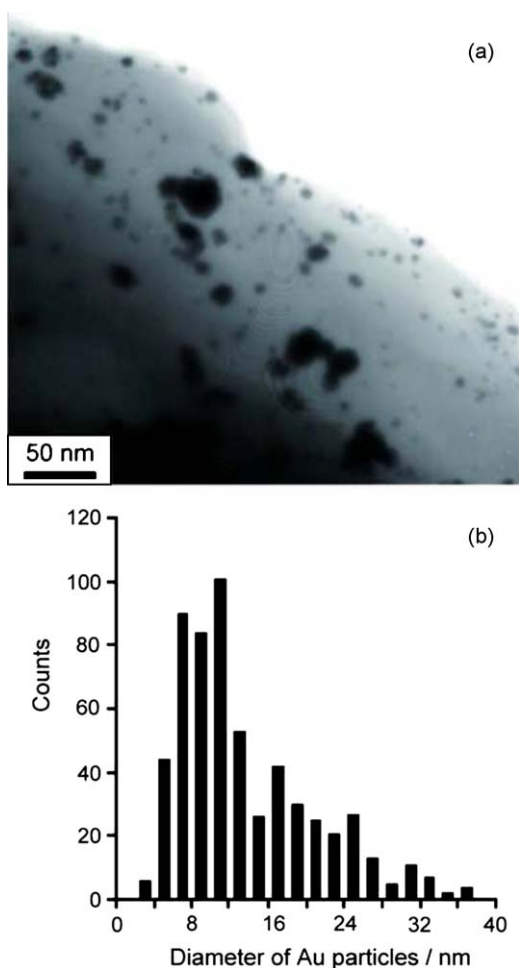

Fig. 2. TEM image (a) and the size distribution (b) of 0.45 wt% Au/cellulose prepared by DR.
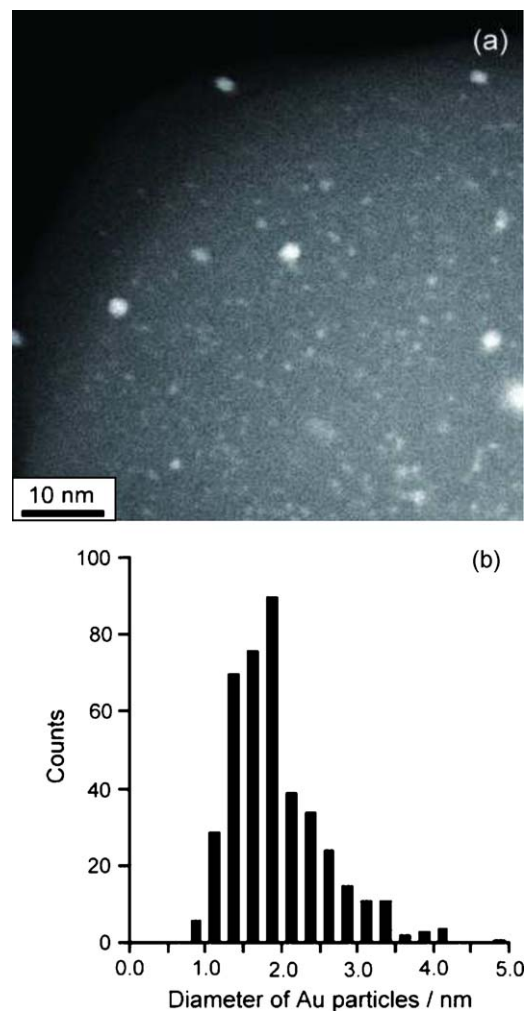

Fig. 3. HAADF-STEM image (a) and the size distribution (b) of 0.23 wt% Au/cellulose prepared by SG.

Table 2
Kinetic properties of different Au catalysts in glucose oxidation.

Entry	Catalyst	Reaction conditions[a]	Au size (nm)	TOF (s^{-1})	E_a ($kJ\,mol^{-1}$)	Reaction order of glucose (a)
1	Au/cellulose	A	2.0 ± 1.0	9.1	–	–
2[b]	Au/NPC	A	2.4 ± 0.8	10	–	–
3	Au/cellulose	B	2.4 ± 1.9	2.0	69	1.5
4[c]	Au/NPC	B	2.4 ± 0.8	2.6	72	1.0
5[c]	Au/Al$_2$O$_3$	B	2.6 ± 0.8	45	27	0.4

[a] Reaction conditions A: 5 wt% glucose aqueous solution, glucose/Au = 16,000 mol/mol, O$_2$ 60 mL/min, 60 °C, pH 9.5. Reaction conditions B: 5 wt% glucose aqueous solution, glucose/Au = 32,000 mol/mol, O$_2$ 120 mL/min, 50 °C, pH 9.0.
[b] Ref. [22].
[c] Ref. [8].

comparable to that of Au/NPC but much lower than that of Au/Al$_2$O$_3$.

4. Discussion

4.1. Direct deposition of gold nanoparticles onto cellulose by solid grinding

Gates and co-workers reported that Me$_2$Au(acac) is initially physisorbed on the metal oxide supports and reacts with surface OH groups of metal oxides followed by the ligand exchange to make dimethyl gold(III) complexes on the oxide surfaces [23–25]. The interaction between physisorbed Me$_2$Au(acac) and surface OH groups by hydrogen bonds was also proposed by DFT calculation [26]. In the SG method, the surface OH groups of glucose unit in cellulose would act as adsorption sites for Me$_2$Au(acac) and the grinding of volatile Me$_2$Au(acac) might promote the direct interactions. Dimethyl gold(III)acetylacetonate adsorbed on cellulose surfaces and the surface OH groups could effectively interact to prevent Au precursors from aggregation, leading to highly dispersed small Au NPs. Although other supports such as porous coordination polymers (500–3000 m^2/g) [14] and metal oxides (20–180 m^2/g) [8] could support over 2 wt% of Au, the amount of Au to be deposited was limited to 0.23 wt% in the case of cellulose. The specific surface area of cellulose used was very small, less than 10 m^2/g, and cellulose OH groups are weak proton donors with respect to metal oxides. Thus, the amount of OH groups to be reacted by ligand exchange or interacted with dimethyl gold(III) complexes by hydrogen bonds were not sufficiently large at the cellulose surfaces. Hence, Me$_2$Au(acac), which was not bounded with the cellulose surfaces, was removed from the cellulose surfaces during the flow of H$_2$ in N$_2$, causing a decrease in the Au content after reduction (entry 3 in Table 1). The addition of a small amount of water during grinding was effective to obtain a certain amount of small Au particles on cellulose. This might provide the adsorption sites for Au(III) complexes by the formation of hydrogen bonds on the cellulose surfaces.

4.2. Aerobic oxidation of glucose over Au/cellulose

Table 2 shows the comparison of TOF values among supported Au catalysts. The TOF value of Au/cellulose was comparable to that of Au/NPC (entries 3 and 4). Activated carbon and carbon materials have been widely used as supports for catalytic metals owing to high specific surface area. Cellulose proved that surface functional groups can stabilize small Au NPs, indicating that high specific surface areas are not always necessary to keep Au particles small. In addition, this work has revealed that Au/cellulose has an appreciably high catalytic performance (22,000 h^{-1} of MTY) for glucose oxidation owing to the existence of Au clusters smaller than 2 nm and the hydrophilic properties of cellulose surfaces, while the MTY for Au NPs with diameters of about 2.4 nm supported on polymer gel was recorded to be only 450 h^{-1} for glucose oxidation at 50 °C and at pH 9.5, as reported by Biffis et al. [12].

Rate dependency on glucose concentration in the presence of excess amounts of O$_2$ (Fig. 4) and apparent activation energy (Fig. 5) were estimated to be 1.5 and 69 kJ mol^{-1}, respectively (entry 3 in Table 2). These values were also similar to those of Au/NPC (entry 4) but higher than those of Au/metal oxides (entry 5) [8] obtained under the same conditions. Taking into consideration that the TOF value of Au/cellulose was about one-twentieth of that of Au/Al$_2$O$_3$ in spite of similar size of Au particles (entry 5) [8], we conclude that glucose oxidation may proceed through different pathways.
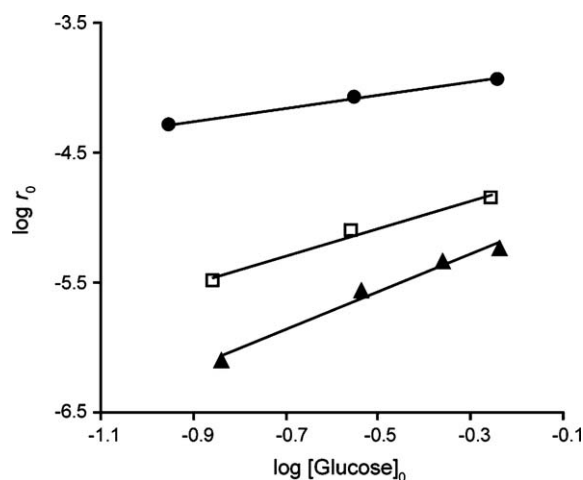

Fig. 4. Rate dependency on glucose concentration. Au/Al$_2$O$_3$: (●) [8]; Au/NPC: (□) [8]; Au/cellulose: (▲). *Conditions*: glucose/Au = 32,000 mol/mol, O$_2$ 120 mL/min, 60 °C. The pH of the solution was kept at 9.0 by titrating 1 M NaOH.
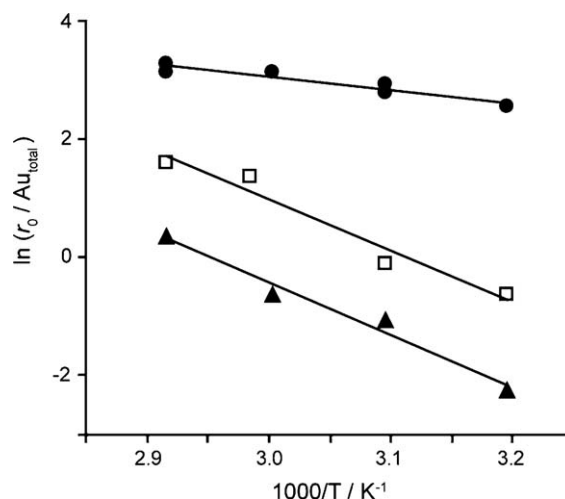

Fig. 5. Arrhenius plots for glucose oxidation. Au/Al$_2$O$_3$: (●) [8]; Au/NPC: (□) [8], Au/cellulose: (▲). *Conditions*: 5 wt% glucose solution, glucose/Au = 32,000 mol/mol, O$_2$ 120 mL/min. The pH of the solution was kept at 9.0 by titrating 1 M NaOH.

In our previous work, we found that the control of the size of Au particles was more critical than the selection of support in the glucose oxidation over metal oxide supported Au catalysts. However, distinct differences between metal oxide supports and carbons were observed in terms of catalytic activity and kinetic behaviors [8]. Gold NPs supported on cellulose showed similar behavior to Au/C. This result suggested that Au NPs on inert supports which have weak or no metal–support interactions more strongly depend on the reaction temperature and the glucose concentration as compared to the case on metal oxide supports.

5. Conclusions

We have demonstrated that Au NPs around 2 nm in diameter can be deposited onto cellulose by the solid grinding method with $Me_2Au(acac)$. Although the amount of Au to be deposited is limited to 0.23 wt% because of the low specific surface area, surface OH groups of cellulose can act as stabilizers to keep Au particles small. Small Au NPs supported on cellulose significantly improved their catalytic activity for glucose oxidation as compared to large Au NPs on cellulose, recording a MTY of $6 \ s^{-1}$ and a TOF of $11 \ s^{-1}$ at 60 °C and at pH 9.5.

Acknowledgements

References

[1] P. Gallezot, Catal. Today 121 (2007) 76–91.
[2] M. Besson, F. Lahmer, P. Gallezot, P. Fuertes, G. Fléche, J. Catal. 152 (1995) 116–121.
[3] A. Abbadi, H. van Bekkum, Appl. Catal. A: Gen. 124 (1995) 409–417.
[4] S. Biella, L. Prati, M. Rossi, J. Catal. 206 (2002) 242–247.
[5] C. Della Pina, E. Falletta, L. Prati, M. Rossi, Chem. Soc. Rev. 37 (2008) 2077–2095, and references therein.
[6] N. Thielecke, M. Aytemir, U. Prüße, Catal. Today 121 (2007) 115–120.
[7] C. Baatz, N. Decker, U. Prüße, J. Catal. 258 (2008) 165–169.
[8] T. Ishida, N. Kinoshita, H. Okatsu, T. Akita, T. Takei, M. Haruta, Angew. Chem. Int. Ed. 47 (2008) 9265–9268.
[9] T. Ishida, M. Haruta, Angew. Chem. Int. Ed. 46 (2007) 7154–7156, and references therein.
[10] H. Miyamura, R. Matsubara, Y. Miyazaki, S. Kobayashi, Angew. Chem. Int. Ed. 46 (2007) 4151–4154.
[11] S. Kanaoka, N. Yagi, Y. Fukuyama, S. Aoshima, H. Tsunoyama, T. Tsukuda, H. Sakurai, J. Am. Chem. Soc. 129 (2007) 12060–12061.
[12] A. Biffis, S. Cunial, P. Spontoni, L. Prati, J. Catal. 251 (2007) 1–6.
[13] T. Ishida, S. Okamoto, R. Makiyama, M. Haruta, Appl. Catal. A: Gen. 353 (2009) 243–248.
[14] T. Ishida, M. Nagaoka, T. Akita, M. Haruta, Chem. Eur. J. 14 (2008) 8456–8460.
[15] K.R. Reddy, N.S. Kumar, P.S. Reddy, B. Sreedhar, M.L. Kantam, J. Mol. Catal. A: Chem. 252 (2006) 12–16.
[16] K.R. Reddy, N.S. Kumar, B. Srredhar, M.L. Kantam, J. Mol. Catal. A: Chem. 252 (2006) 136–141.
[17] J. He, T. Kunitake, A. Nakao, Chem. Mater. 15 (2003) 4401–4406.
[18] A. Corma, P. Concepción, I. Domínguez, V. Fornés, M.J. Sabater, J. Catal. 251 (2007) 39–47.
[19] T. Ishida, K. Kuroda, N. Kinoshita, W. Minagawa, M. Haruta, J. Colloid Interface Sci. 323 (2008) 105–111.
[20] K. Kuroda, T. Ishida, M. Haruta, J. Mol. Catal. A: Chem. 298 (2009) 7–11.
[21] B.P. Block, J.C. Bailar Jr., J. Am. Chem. Soc. 73 (1951) 4722–4725.
[22] H. Okatsu, N. Kinoshita, T. Akita, T. Ishida, M. Haruta, Appl. Catal. A: Gen. 369 (2009) 8–14.
[23] J. Guzman, B.C. Gates, Langmuir 19 (2003) 3897–3903.
[24] J.C. Fierro-Gonzalez, Y. Hao, B.C. Gates, J. Phys. Chem. C 111 (2007) 6645–6651.
[25] Y. Hao, B.C. Gates, J. Catal. 263 (2009) 83–91.
[26] M. Okumura, S. Tsubota, M. Haruta, J. Mol. Catal. A: Chem. 199 (2003) 73–84.