Chemistry Letters Vol.32, No.9 (2003)

Direct Production of Hydrogen Peroxide from H_2 and O_2 over Highly Dispersed Au catalysts

Mitsutaka Okumura,* Yasutaka Kitagawa, Kizashi Yamagcuhi, Tomoki Akita,† Susumu Tsubota,†† and Masatake Haruta††
Department of Chemistry Graduate School of Science Osaka University, 1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043
†*Special Division of Green Life Technology, National Research Institute of Advance Technology and Science, 1-8-31 Midorigaoka, Osaka 563-8577*
††*Research Institute for Green Technology, National Research Institute of Advance Technology and Science, 1-1-1 Higashi, Ibaraki 305-8565*

(Received June 12, 2003; CL-030532)

Highly dispersed Au catalysts were active for the direct formation of H_2O_2 form H_2 and O_2. Especially, the rate of H_2O_2 production greatly increased when Au nanoparticles were deposited onto SiO_2, MCM-41 and active carbon supports.

It is well known that H_2O_2 is a highly selective oxidant in the industrial process and is an environment-friendly agent. The current process for the commercial production of H_2O_2 is a sequential hydrogenation and oxidation of an alkyl anthraquinone.[1] However, this process has the disadvantages of organic solvent contamination toward aqueous peroxide solution and the periodic replacement of anthraquinone due to hydrogenation. In the aim to explore less expensive and environmentally friendly route, studies have been focused onto the direct production of H_2O_2 from H_2 and O_2 over a supported noble metal catalyst. Supported Pd catalysts have been studied over the last two decades.[2–5] On the other hand, Sellers and co-workers proposed that Au was one of the favorable materials for the production of H_2O_2.[6] Lately, H_2O_2 syntheses over Au and Pd–Au catalysts were reported.[7–9] However, the detail investigation of the catalytic properties of Au catalysts, such as support effect, size effect of deposited Au nano-particles is not carried out.

In this work, deposition-precipitation (DP) and gas-phase grafting (GG) methods are used for depositing Au on several supports. The detail of the preparation conditions and the experimental setup were described elsewhere.[10–15] As Au precursors for DP and GG methods, $HAuCl_4$ and $(CH_3)_2Au(CH_3COCHCOCH_3)$, abbreviated to $Me_2Au(acac)$, were used, respectively. All the initial loading of Au was adjusted to be 1 wt %. The support used are MgO (UBE Co. Ltd., 140 m^2/g), Al_2O_3 (a reference sample of the Catalysis Society of Japan, JRC-ALO7,180 m^2/g), SiO_2 (Merck, silica gel 60 extra pure, 400 m^2/g), TiO_2 (Degussa, P-25, 56 m^2/g), ZrO_2 (JRC-ZRO-3, 94.4 m^2/g), Active carbon (Kansai coke and Chemicals Co. Ltd., Maxsorb., 2000 m^2/g), SiO_2–Al_2O_3 (JRC-SAH-1, 240 m^2/g), and MCM-41 (mesopore widths; 2.7 nm, ca. 1000 m^2/g).

Catalytic activity measurements were carried out using a TAIATSU Co. Ltd. hard glass autoclave with polycarbonate cylinder. Water was used for the solvent and the pH of the solvent was adjusted by use of NaOH or HCl solutions. Its nominal volume is 100 mL and its maximum working pressure is 2.0 MPa. The autoclave was stirred with a magnetic stirrer. The reaction temperature was ranging from 278 to 298 K and the induced pressure was ranging from 0.0 to 1.0 MPa. The gases, oxygen and hydrogen (molar ratio; 3:7, SV = 8000 mL/g-cat. h^{-1}), were allowed to flow through a fine glass frit at the bottom of the reactor. The reaction time was 2 h. Small aliquots of reaction mixture were withdrawn with syringe to be analyzed by colorimetry after complexation with a $TiOSO_4/H_2SO_4$ reagent.

Table 1. Formation of H_2O_2 from the reaction H_2 and O_2 over Au/catalysts

Sample[a]	Prep. Method	Pressure[b] /MPa	$R[H_2O_2]^c$ /mmol $(g\text{-cat.})^{-1}$ h^{-1}
Au/MgO	DP	0.1	0.000
Au/TiO_2	DP	0.1	0.152
		0.5	0.593
		1.0	0.798
Au/Al_2O_3	DP	0.1	0.147
		0.5	0.342
		1.0	0.418
Au/ZrO_2	DP	0.1	0.147
Au/SiO_2	GG	0.1	0.265
		0.5	0.854
		1.0	1.601
Au/SA[d)]	GG	0.1	0.044

[a]Calcined at 673 K for 4 h in air. [b]Absolute pressure. [c]reaction temperature was 288 K. [d]Au/SiO_2–Al_2O_3.

H_2O_2 production from H_2 and O_2 over Au deposited on several type of metal oxide were examined. The results were summarized in Table 1. All the pH of solvents was 6. The rates of H_2O_2 formation over Au/MgO and Au/SiO_2–Al_2O_3 were extremely low. As MgO and SiO_2–Al_2O_3 are typical basic and acidic metal oxides, respectively, it suggests that the basic and acidic metal oxides are not suitable for the support of Au catalysts in H_2O_2 formation. On the other hand, it was found that Au/SiO_2 showed the highest rate of H_2O_2 formation than those of the other Au catalysts while the H_2O_2 conversions from H_2 under 0.1, 0.5, and 1.0 MPa conditions were 0.11, 0.34, 0.64%, respectively. Additionally, it was found that the rate of H_2O_2 production over Au/SiO_2 was decreased in both more acidic and basic conditions. It is well known that the catalytic activity of Au catalysts is greatly dependent on the selection of the support and the size of Au nanoparticles deposited. Especially, the support, such as TiO_2, which have strong metal-support interaction, exhibits extremely high CO oxidation catalytic activity at below room temperature. However, the rate of H_2O_2 formation over highly dispersed Au/TiO_2 catalyst was not so high. This suggested that the competition between H_2O_2 formation and H_2O_2 decomposition took place. From the H_2O_2 decomposition experiments, it was confirmed that the decomposition rate of H_2O_2 over Au/TiO_2 was increased with a decrease of the mean diameter of Au deposited on TiO_2. This is probably because the perimeter between Au and TiO_2 that is an active site in oxidative reactions decomposes H_2O_2 and activates oxygen strongly and produces water from H_2 and O_2. This means that the inert support which has relatively weak Au-support interaction is suitable for this reaction. Therefore, we concluded that SiO_2 was favorable for the metal oxide support of Au catalyst in H_2O_2 production. It was also found that Au/SiO_2 showed higher rate of H_2O_2 formation under the pressurized condition.

Next the H_2O_2 productions over Au/MCM-41 and Au/SiO_2 catalysts with different mean diameter of Au nanoparticles deposited were examined in order to elucidate the size effect of Au nanoparticles in H_2O_2 production. The obtained results were listed in Table 2. It was found that the rate of H_2O_2 formation was decreased with an increase of the mean diameter of Au nanoparticles. This tendency was also confirmed by the experimental result that Au/SiO_2 prepared by IMP method whose mean diameter of Au particles was about 30 nm produced no H_2O_2. Thus, it is obvious that the high dispersion of Au nanoparticles onto the support is essential to presenting high catalytic activity in H_2O_2 formation over Au catalysts.

Table 2. Formation of H_2O_2 from the reaction H_2 and O_2 over Au/SiO_2 and Au/MCM-41 prepared by GG at different calcinations temperatures

Support	Method	Calc. temp.[a] /K	D_{Au}[b] /nm	$R[H_2O_2]$[d] /mmol (g-cat. h)$^{-1}$
Au/MCM-41	GG	400	5.0 ± 2.0	0.451
Au/SiO_2	GG	400	9.2 ± 3.3	0.265
		600	10.3 ± 3.3	0.223
		800	11.6 ± 3.6	0.214
	IMP	400	30[c)]	0.000

[a]Calcined for 4 h in air. [b]TEM observation. [c]XRD. [d]Reaction temperature was 288 K.

Table 3. Formation of H_2O_2 from the reaction H_2 and O_2 over Au/AC and Au/MCM-41 prepared by GG

Sample[a]	Prep. Method	Pressure[b] /MPa	$R[H_2O_2]$[c] /mmol (g-cat.)$^{-1}$ h^{-1}
Au/AC	GG	0.1	0.270
		0.5	1.261
		1.0	1.907
	IMP	0.1	0.0
Au/MCM-41	GG	0.1	0.451
		0.5	1.350
		1.0	2.113

[a]Calcined at 673 K for 4 h in air. [b]Absolute pressure. [c]Reaction temperature was 288 K.

From these experiments, it was found that the size of Au particles deposited and the selection of the inert support were the important factors to achieve the high yield of H_2O_2 formation form H_2 and O_2 over Au catalysts. As active carbon (AC) is the one of the inert supports, the highly dispersed Au/AC catalyst could be an active catalyst in H_2O_2 production. In the next, Au/AC catalysts prepared by IMP and GG methods were examined. As shown in Figure 1, Au nanoparticles with a diameter less than 10 nm were highly dispersed on the surface of AC by GG method. The obtained experimental results were listed in Table 3. The rate of H_2O_2 formation at ambient condition over Au/AC prepared by GG is as much as that over Au/SiO_2 prepared by GG. On the other hand, Au/AC prepared by IMP was much less active than Au/AC prepared by GG. This is due to the low dispersion of Au particles deposited on AC. Therefore, the importance of the above mentioned factors were reconfirmed in these experiments.

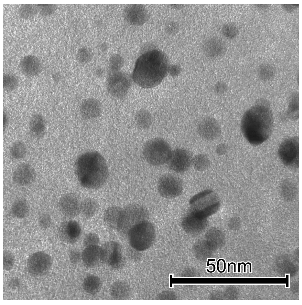

Figure 1. TEM image of Au/AC prepared by GG and calcined in air at 673 K for 4 h.

In conclusion, this communication reports that the Au/AC, Au/MCM-41, and Au/SiO_2 catalysts prepared by GG are very active for direct production of H_2O_2 from H_2 and O_2. It is concluded that the two factors that the size of Au nanoparticles deposited on the support and the selection of the inert support, such as AC, MCM-41, and SiO_2, are indispensable to obtain active Au catalysts in H_2O_2 production.

References

1 W. T. Hess, in "Kirk-Othmer Encyclopedida of Chemical Technology," ed. by J. I. Kroschwitz and M. Howe-Grant, Wiley, New York (1995), Vol. 13, p 961.
2 L. W. Gosser, U. S. Patent 5135731 (1992).
3 L. W. Gosser and J.-A. T. Schwartz, U. S. Patent 4832938 (1989).
4 Y. Izumi, H. Miyazaki, and S. Kawahara, U. S. patent 4009252 (1977).
5 D. P. Dissanayake and J. H. Lunsford, *J. Catal.*, **206**, 173 (2002).
6 P. P. Olivera, E. M. Patrito, and H. Sellers, *Surf. Sci.*, **313**, 25 (1994).
7 P. Landon, P. J. Collier, A. F. Carley, D. Chadwick, A. J. Papworth, A. Burrows, C. J. Kiely, and G. J. Huchings, *Phys. Chem. Chem. Phys.*, **5**, 1917 (2003).
8 T. Ishihara, R. Ando, H. Nishiguchi, and Y. Takita, Presented at the 87rd Annual Meeting of Catalysis Society of Japan, Suita, March 2001, Abstr., No. 1P40.
9 K. Otsuka and I. Yamanaka, *Electrochim. Acta*, **35**, 319 (1990).
10 H. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, and B. Delmon, *J. Catal.*, **144**, 175 (1993).
11 M. Haruta, N. Yamada, T. Kobayashi, and S. Iijima, *J. Catal.*, **115**, 301 (1989).
12 M. Okumura, K. Tanaka, A. Ueda, and M. Haruta, *Solid State Ionics*, **95**, 143 (1997).
13 M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma, and M. Haruta, *Catal. Lett.*, **51**, 53 (1998).
14 M. Okumura, S. Tsubota, M. Iwamoto, and M. Haruta, *Chem. Lett.*, **1998**, 315.
15 M. Okumura, S. Tsubota, and M. Haruta, *J. Mol. Catal. A: Chem.*, **199**, 73 (2003).