Pd–Au Bimetal Supported on Rutile–TiO_2 for Selective Synthesis of Hydrogen Peroxide by Oxidation of H_2 with O_2 under Atmospheric Pressure

Tatsumi Ishihara,*[1] Yuiko Hata,[1] Yohei Nomura,[1] Kenji Kaneko,[2] and Hiroshige Matsumoto[1]
[1]*Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395*
[2]*Department of Materials Sciences and Engineering, Faculty of Engineering, Kyushu University,*
744 Motooka, Nishi-ku, Fukuoka 819-0395

(Received April 11, 2007; CL-070394; E-mail: ishihara@cstf.kyushu-u.ac.jp)

Rutile TiO_2 support is effective for increasing the formation rate as well as selectivity to H_2O_2. A great enhancement in the H_2O_2 formation rate and selectivity is achieved by controlling the particle size of Pd–Au (7:3 in weight ratio) alloy, and the average size of 18 nm exhibits the high selectivity to H_2O_2 under atmospheric pressure.

Hydrogen peroxide (H_2O_2) is currently synthesized by using anthraquinone as an intermediate from hydrogen and oxygen.[1] Since this process is composed of multistep reactions, it requires a relatively large energy input to produce H_2O_2 so that the production costs of H_2O_2 become high as an oxidant for the industrial processes. In addition, H_2O_2 is unstable and easily decomposes, and so this reagent is not suitable for transportation. Therefore, there are strong demands for the development of the on-site H_2O_2 synthesis process by the direct oxidation of H_2 with gaseous oxygen. It is reported that Pd catalyst is highly active in the direct synthesis of H_2O_2 from H_2.[2–4] On the other hand, Au is also reported as the active in this direct synthesis of H_2O_2 from H_2[5–7] (in CH_3OH/H_2O liquid), albeit the low selectivity. Furthermore, Au–Pd alloy supported on Al_2O_3 or TiO_2 could be another candidate for the catalyst of H_2O_2 formation,[6,8] and it was reported that TiO_2 exhibits positive support effects on H_2O_2 formation.[6] However, the effects of crystal phase of TiO_2 are not studied in details. It is also reported that the addition of Pd to Au is effective for increasing the H_2O_2 formation rate.[9] In addition to these, there are several numbers of reports on the direct H_2O_2 synthesis from H_2,[10,11] however, large part of the conventional studies on direct synthesis of H_2O_2 were performed under pressurized conditions. H_2O_2 selectivity is not high enough ($<$ ca. 80%) so far. In addition, accumulation of H_2O_2 to high concentration by the partial oxidation of H_2 with O_2 is difficult because of the high activity of H_2O_2 against H_2. Therefore, in order to apply H_2O_2 synthesis from H_2 to the industrial process, high selectivity to H_2O_2 as well as high concentration of H_2O_2 is strongly demanded. In this study, the selective synthesis of H_2O_2 by oxidation of H_2 is achieved by choosing a suitable TiO_2 support for the Pd–Au particle sizes.

Palladium–gold catalyst supported on TiO_2 was prepared by using the conventional incipient wetness techniques using $HAuCl_4$ and $PdCl_2$. The amount of loaded Pd–Au metal was always 1.7 wt %, and the composition of Pd:Au is 82:18 in molar ratio, if not mentioned. Thus, obtained catalyst (1 g, metal content: 25.5 mg) was suspended in deionized water (pH 6, 100 mL), and the gaseous mixture of H_2 and O_2 at each feed rate of 50 mL/min was fed into catalyst suspending water at 283 K. Before addition of catalyst, HCl of 84 mmol/L and H_2SO_4 of 0.368 mol/L were always added for controlling pH and amount of Cl^- ion. The amount of formed H_2O_2 was analyzed by the UV absorption method which is used $TiO(SO_4)$ as the pigment. The selectivity to H_2O_2 is defined as H_2O_2 formation rate divided by H_2 consumption rate. Metal dispersion was measured with the H_2 adsorption isotherm (up to 90 kPa) by using a conventional volumetric gas adsorption system (Nippon Bell, Belsorb SP-18) at 298 K. Chemisorption amount was estimated by subtracting the second adsorption amount from that of the initial one. It is noted that absorption of H_2 into Pd bulk is negligibly small at 298 K and even though it occurs, it can be neglected by the compensation for the first adsorption amount with that of second one.

The support oxides play important roles for the formation rate of H_2O_2, in particular, TiO_2 showed a positive effect among the examined support oxides. Since the morphology and surface composition of Pd–Au particles could easily be affected by the crystal structure of TiO_2 owing to the lattice mismatch and the surface area, the effects of crystal phases of TiO_2 on the H_2O_2 synthesis were investigated. Table 1 summarizes the formation rate and the selectivity of H_2O_2 using the Pd–Au bimetallic alloy on TiO_2 support. It was seen that the formation rate and the selectivity were strongly dependent on the crystal phase of TiO_2. The selectivity reached 78% in the case of Pd–Au alloy supported on P-25 TiO_2, which is the mixed phase of anatase and rutile with the large surface area 40.2 m^2/g. On the other hand, the high formation rate of 22.1 $mmol\,L^{-1}\,h^{-1}$ is achieved in spite of the small surface area (2.0 m^2/g) when rutile TiO_2 was used for the support, whereas the low formation rates, 16.5 $mmol\,L^{-1}\,h^{-1}$, with similar BET surface area (2 m^2/g) when anatase was used. XPS measurement suggests that the

Table 1. Effects of crystal phase of TiO_2 support on H_2O_2 formation rate

Support	H_2 Conversion /%	Selectivity /%	H_2O_2 formation rate /$mmol\,L^{-1}\,h^{-1}$	BET surface area /$m^2\,g^{-1}$	Surface Au/Pd ratio in weight
P-25[a]	1.7	78.4	14.7	40.2	1.076
Anatase	3.9	51.1	16.5	1.6	0.521
Rutile	2.6	62.3	22.1	2.0	1.191

[a]Mixed phase of rutile and anatase, Catalysis Society of Japan reference catalyst, Pd:Au = 44:56 (molar ratio), NaCl: 84 mmol/L, H_2SO_4: 0.368 mol/L, H_2 feed rate: 50 mL/min, O_2 feed rate: 50 mL/min, Metal loading; 1.7 wt %.

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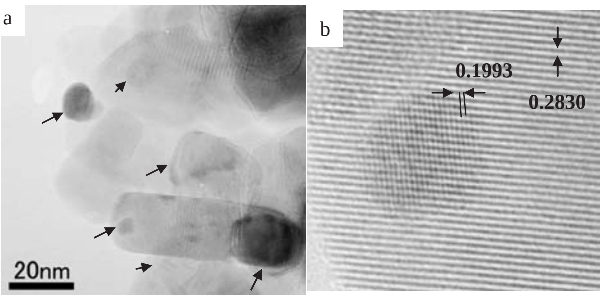

Figure 1. TEM images of Pd–Au supported on rutile TiO_2: (a) Low magnification image, (b) high resolution image. Metal is pointed by arrows.

surface composition was also sensitively varied with the crystal phase of TiO_2 support, and the surface enrichment of Au was observed in case of rutile TiO_2 or P-25 and Pd in case of anatase TiO_2 for support.

Metal particle size is another important factor for increasing the formation rate; however, up to now, there is no detail study on the particle size effects on the H_2O_2 synthesis. In this study, particle size of Pd–Au was controlled by changing the surface area of rutile support. Figure 1 shows the TEM images of Pd–Au particles supported on rutile. Although some distribution in particle sizes was observed, Pd–Au particles distributes between few nm to 30 nm. The estimated particle size by TEM observation was almost the same with that estimated by H_2 chemisorption amount. High-resolution image of Pd–Au particle is also shown in Figure 1b. From the lattice image of TiO_2 support, the observed layer distance is 0.293 nm, which is close to *c* lattice length of rutile (0.29592 nm). Therefore, the electron beam is inserted from [001] direction of rutile TiO_2. On the other hand, the Pd–Au particles tends to be a rectangular shape which reflects on the fcc lattice. The plane distance estimated from this image is 0.199 nm, which is larger than that of (002) plane distance of Pd (0.1941 nm) but smaller than that of Au (0.2039 nm). Therefore, obviously, Au and Pd forms alloy with fcc structure. In addition, as shown in Figure 1b, clear lattice image suggests that the particle is oriented to (002) plane on *c* lattice of rutile TiO_2. Since the always same lattice image is observed on rutile TiO_2, rutile may be effective for exposing {102} Pd–Au or {010} Pd–Au plane for the surface by minimizing the lattice mismatch. This seems to be the origin of positive effects on H_2O_2 formation rate from H_2 and O_2.

Table 2. Effects of average particle size on H_2O_2 formation rate and selectivity[a]

Average particle size/nm	BET Surface area/$m^2\,g^{-1}$	H_2O_2 formation rate/mmol $L^{-1}\,h^{-1}$	Selectivity /%
17.4	76.0	49.2	95.7
18.3	45.5	71.0	99.7
21.7	29.8	64.0	90.8
31.1	2.0	62.8	97.2

[a] W/F = 6 g-cat.h/mol, values at 2 h after reaction started, Pd:Au = 82:18 (molar ratio), Total metal loading: 1.7 wt %, HCl: 84 mmol/L, and H_2SO_4: 0.368 mol/L.

Table 2 shows effects of particle size on the H_2O_2 formation rate and its selectivity. The average metal particle size is estimated by hydrogen chemisorption. Since H_2O_2 formation rate and selectivity increases with increasing Pd content and these become the highest at Pd:Au = 82:18, effects of particle size were measured on this composition. The H_2O_2 formation rate increased with decreasing the particle sizes then reached the maximum at the average particle size of ca. 18 nm. In addition, at this particle size, the selectivity was as high as 99.7% with 3.5% yield of H_2O_2. Considering the atmospheric pressure in this study, the formation rate of H_2O_2, 71.0 mmol $L^{-1}\,h^{-1}$, is high. Although the reaction condition is quite different and it can not be simply compared, the H_2O_2 productivity in this study under atmospheric pressure is 189.8 $mol_{H2O2}/h\,kg_{cat.}$, which is almost the same with that (202 mol $H_2O_2/h\,kg_{cat.}$) of the reported maximum value[6] under pressurized condition (14 MPa); however, selectivity to H_2O_2 is much higher in this study. Since the H_2O_2 is quite unstable and easy to decompose, this ca. 100% selectivity to H_2O_2 is highly interesting and this high selectivity can be sustained over a few hours after reaction started (up to 0.5 wt %). In addition, 80% selectivity is sustained up to 0.8 wt % after 6 h. The amount of H_2O_2 concentration monotonically increased with the reaction time and it attained a value of 0.9 wt % after 8 h. This study demonstrated that the high formation rate and the selectivity could be achieved under the atmospheric pressure by controlling the particle size and the surface structure of Pd–Au by lattice matching with rutile TiO_2. This size controlled Pd–Au alloy on rutile TiO_2 may lead to a new on-site H_2O_2 synthesis process.

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