Pd–Au Bimetal Supported on Rutile–TiO₂ for Selective Synthesis of Hydrogen Peroxide by Oxidation of H₂ with O₂ under Atmospheric Pressure

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Rutile TiO₂ 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 (H₂O₂) 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 H₂O₂ become high as an oxidant for the industrial processes. In addition, H₂O₂ 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 H₂O₂ synthesis process by the direct oxidation of H₂ with gaseous oxygen. It is reported that Pd catalyst is highly active in the direct synthesis of H₂O₂ from H₂.²⁻⁴ 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 CH₃OH/H₂O liquid), albeit the low selectivity. Furthermore, Au-Pd alloy supported on Al₂O₃ or TiO₂ could be another candidate for the catalyst of H₂O₂ formation,^{6,8} and it was reported that TiO₂ exhibits positive support effects on H₂O₂ formation.⁶ However, the effects of crystal phase of TiO₂ are not studied in details. It is also reported that the addition of Pd to Au is effective for increasing the H₂O₂ 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 H₂O₂ were performed under pressurized conditions. H₂O₂ 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 H₂O₂ synthesis from H₂ to the industrial process, high selectivity to H2O2 as well as high concentration of H₂O₂ is strongly demanded. In this study, the selective synthesis of H_2O_2 by oxidation of H_2 is achieved by choosing a suitable TiO₂ support for the Pd–Au particle sizes.

Palladium-gold catalyst supported on TiO2 was prepared by using the conventional incipient wetness techniques using HAuCl₄ and PdCl₂. 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 H₂ and O₂ 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 H₂SO₄ of 0.368 mol/L were always added for controlling pH and amount of Cl⁻ ion. The amount of formed H₂O₂ was analyzed by the UV absorption method which is used TiO(SO₄) as the pigment. The selectivity to H₂O₂ is defined as H₂O₂ formation rate divided by H₂ consumption rate. Metal dispersion was measured with the H₂ 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 H₂ 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 H₂O₂, in particular, TiO₂ 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 TiO2 owing to the lattice mismatch and the surface area, the effects of crystal phases of TiO₂ on the H₂O₂ synthesis were investigated. Table 1 summarizes the formation rate and the selectivity of H₂O₂ using the Pd-Au bimetallic alloy on TiO₂ support. It was seen that the formation rate and the selectivity were strongly dependent on the crystal phase of TiO₂. The selectivity reached 78% in the case of Pd-Au alloy supported on P-25 TiO₂, which is the mixed phase of anatase and rutile with the large surface area $40.2 \text{ m}^2/\text{g}$. 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 $(2.0 \text{ m}^2/\text{g})$ when rutile TiO₂ was used for the support, whereas the low formation rates, 16.5 mmol L^{-1} h⁻¹, with similar BET surface area (2 m²/ 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

^aMixed 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 %.



Figure 1. TEM images of Pd–Au supported on rutile TiO₂: (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 H₂ chemisorption amount. High-resolution image of Pd-Au particle is also shown in Figure 1b. From the lattice image of TiO₂ 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 TiO₂. 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 TiO₂. Since the always same lattice image is observed on rutile TiO₂, 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 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

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

Average particle	BET Surface	H ₂ O ₂ formation	Selectivity
size/nm	$area/m^2 g^{-1}$	rate/mmol $L^{-1} h^{-1}$	/%
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

 $^{a}W/F = 6 \text{ g-cat.h/mol}$, values at 2 h after reaction started, Pd:Au = 82:18 (molar ratio), Total metal loading: 1.7 wt %, HCl: 84 mmol/L, and H₂SO₄: 0.368 mol/L.

study under atmospheric pressure is 189.8 mol_{H2O2}/hkg_{cat}, which is almost the same with that $(202 \text{ mol } H_2O_2/h \text{ kg}_{cat})$ of the reported maximum value⁶ 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 H₂O₂ 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 TiO₂. This size controlled Pd-Au alloy on rutile TiO2 may lead to a new on-site H₂O₂ synthesis process.

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