Outmost surface analysis of Pd-Au nanocolloid for synthesis of high concentration H_2O_2 by direct oxidation of H_2

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Abstract: Synthesis of high concentration H_2O_2 by direct oxidation of H_2 was studied on Pd-Au nano colloid under a high P_{O2} condition. Although the concentration of H_2O_2 achieved is lower than 1wt% in the conventional study, it was found that H_2O_2 concentration could be accumulated up to 11wt% after 20 h under P_{O2}=80% on Pd-Au nano colloid. The mechanism of high concentration H_2O_2 achieved under high P_{O2} condition was investigated with low energy ion scattering (LEIS) measurement and it was found that the high concentration of Br on the Pd-Au colloid surface was sustained resulting in the suppression of H_2O_2 decomposition.

Keywords: H_2O_2 synthesis, Nano colloid, Surface analysis.

1. Introduction

Demands for hydrogen peroxide (H_2O_2) are increasing currently with the increasing importance of green chemistry. Therefore, the market for H_2O_2 is expanding in various fields such as breaching etc. At present, H_2O_2 is synthesized by the so-called anthraquinone method, which is consisted of antraquinone hydrogenation followed by the auto-thermal oxidation of hydroantraquinone. On the other hand, the direct synthesis of H_2O_2 from gaseous hydrogen and oxygen is attracting much interest as a simple H_2O_2 production method, in particular, for the small scale production, because of high production rate and simple process [1]. Studies of various catalysts, particularly Pd- and Pt-based catalysts, have been conducted. In this study, the effects of the reaction condition on H_2O_2 formation rate on Pd-Au nano colloid which shows high yield of H_2O_2 in our previous study [2] were investigated, in particular, under high P_{O2} condition. In order to understand the high H_2O_2 concentration achieved, outmost surface of Pd-Au colloid after reaction was also studied. Although it is well known that addition of Br is highly important for achieving the high selectivity to H_2O_2 in direct oxidation method, performance of Br under reaction condition is not clearly understand up to now. In this study, we applied low energy ion scattering techniques for the analysis of outmost surface of Pd-Au nano colloid.

2. Experimental

Pd-Au bimetal nano colloid was prepared by the chemical reduction of $HAuCl_4$ and $PdCl_2$ in a mixture of 1ml of 5.6 M HCl solution, 25 ml of H_2O, 25 ml of C_2H_5OH and 1 g of oxalic acid. The total amount of Pd and Au was maintained at 50 μmol and the Pd:Au ratio was maintained at 60:40 mol% for the catalyst. In order to mono dispersion of the colloid, 0.43 g of polyvinylpyrrolidone (PVP, Kishida Pure Chem. Co. Ltd.) was added for preventing aggregation of nano colloid and heated with microwave oven(353K, 0.5h). The synthesis of H_2O_2 from a gaseous mixture of H_2 and O_2 was tested in a stainless steel autoclave reactor with a magnetic stirring condition at 283 K, 1MPa. This reactor was charged with an aqueous solution containing a catalyst comprising 17.8 mg in total concentration of Pd and Au, for experiments performed under all conditions used. Gaseous mixture of H_2-O_2-N_2 was fed through a porous glass filter (pore size, 10 μm in diameter) and the catalyst suspension was stirred mechanically at 1000 rpm using a motor. A back pressure valve (TESCOM type 2500) was used for pressurizing the reactor and thermal flow controller were used for gas flow rate control. The amount of H_2O_2 formed was analyzed by the redox titration method and the amounts of gaseous H_2 and O_2 were measured with a TCD gas chromatograph (Shimadzu GC 8A). The selectivity of H_2 to H_2O_2 was defined as the H_2O_2 formation rate divided by the H_2 consumption rate.

Samples for LEIS measurement were prepared by drying the colloidal solution on a clean glass plate at 333 K and the commercial equipment (Q-tac, Ion-Toff).

3. Results and discussion

Figure 1 shows time dependence of H_2O_2 accumulated amount under different P_{O2} at 298 K and P_{H2}=10 %. At initial period, H_2O_2 was selectively formed (H_2O_2 yield is higher than 70%), however, with increasing H_2O_2 concentration, formation rate of H_2O_2 became later and after ca. 10h, H_2O_2 concentration was almost independent of reaction time. This means that no H_2O_2 was formed after 10 h suggesting that the catalyst became deactivated or formation rate of H_2O_2 was balanced with decomposition rate. As shown in Fig.1, the amount of H_2O_2 concentration achieved was increased with increasing P_{O2} for H_2O_2 synthesis and at P_{O2}=80 %, the amount of H_2O_2 was achieved to ca. 11wt% which is largest in the open literature. Therefore, high oxygen partial pressure for H_2O_2 synthesis is suitable for achieving the high concentration of H_2O_2 obtained.

The mechanism of high H_2O_2 concentration obtained under high oxygen partial pressure was further studied. As shown in Fig.1, the initial H_2O_2 formation rate was hardly influenced with oxygen partial pressure in reactant. In addition, it was found that H_2O_2 decomposition rate was decreased with increasing oxygen partial pressure in reactant. Therefore, high H_2O_2 concentration obtained under high P_{O2} can be assigned to the suppression of H_2O_2 decomposition with H_2. The mechanism of suppressed H_2O_2 decomposition was further studied. Figure 2 shows surface Br concentration estimated by LEIS analysis. Since the amount of Br is small and Br was localized on the surface, detection of Br was hardly performed by XPS and so we used LEIS for analysis of Br. As shown in Figure 2, the amount of surface Br is almost the same at initial reaction period, however, after 10 h, when P_{O2} is high, high concentration of Br is sustained and so this could explain the suppression of H_2O_2 decomposition when P_{O2} is high in reactant. Since Pd-Au nano colloid became reduced state with reaction time, high P_{O2} in reactant keep the high oxygen and Br concentration on the surface resulting in the high H_2O_2 formation rate sustained under the high H_2O_2 concentration condition.

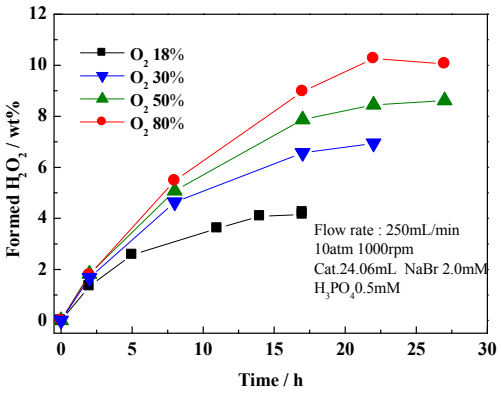

Figure 1 H_2O_2 concentration as a function of reaction time on Pd-Au nano colloid

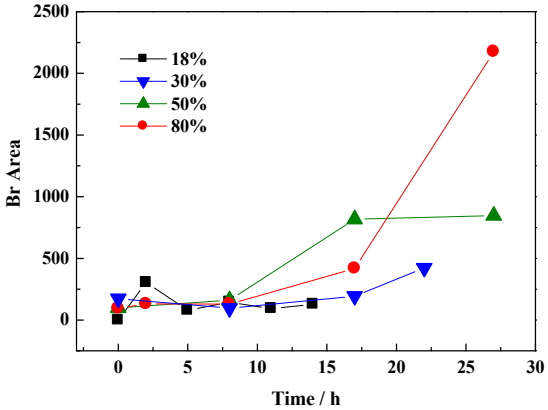

Figure 2 Br peak area in LEIS spectra as a function of reaction period.

4. Conclusions

Effects of oxygen partial pressure on H_2O_2 direct synthesis on Pd-Au nano colloid were investigated in this study and it was found that H_2O_2 concentration accumulated was increased with increasing oxygen partial pressure and at 80 % P_{O2}, H_2O_2 concentration was achieved to 11 wt% in 270 cc reactor after 20h. This positive effects of P_{O2} was explained by high Br concentration sustained on the surface with increasing P_{O2}.

References

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