Pd/Graphite as a Superior Catalyst for the Direct Synthesis of Hydrogen Peroxide from H_2 and O_2

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Graphite was found to be a superior support for Pd catalyst for the direct synthesis of H_2O_2 from H_2 and O_2. The Pd/graphite catalyst prepared by HCHO reduction showed much higher H_2O_2 formation activity and selectivity than that prepared by impregnation. The size and morphology of Pd nanoparticles may play roles in H_2O_2 formation. The worm-like small Pd nanoparticles over graphite surfaces exhibited higher catalytic performances in H_2O_2 formation.

Hydrogen peroxide is one of the most essential chemicals for pulp/paper bleaching, water treatment and chemical production, and the demand for H_2O_2 is growing significantly because of its green character. In the current chemical industry, H_2O_2 is mainly produced by the multistep anthraquinone process, which suffers from several drawbacks, such as use of complex and toxic solvent, requirements of several energy-intensive steps, and high investment and operating costs. Therefore, the direct synthesis of H_2O_2 from H_2 and O_2, which is a more economic and greener route, has attracted much attention in recent years.[1–4] Some effective catalysts or intriguing systems have been reported for H_2O_2 direct synthesis,[5] and there is a consensus that supported Pd catalysts are most efficient for this reaction.[1–4] However, there is still no sufficient insight into excellent supports. So far, silica and charcoal have been most widely used as supports for Pd catalysts for H_2O_2 direct synthesis.[1–4] Clearly, there is a need for developing more effective supports for Pd catalysts. Moreover, many fundamental aspects such as the effect of size and morphology of Pd still remain ambiguous.

Recently, we found that graphite could function as a very efficient support for Pd catalyst for H_2O_2 direct synthesis. Herein, we report the catalytic behaviors of the Pd/graphite catalyst and the effect of preparation method on catalytic performance. The effect of size and morphology of Pd will also be discussed through studies of Pd/graphite catalysts prepared by different methods.

Pd catalysts loaded on various supports were prepared by either impregnation or chemical reduction using HCHO as a reductant. For impregnation, the support was added to acidic aqueous $PdCl_2$ solution, and then water was removed by evaporation after stirring for 8 h. The dried powder was calcined in air at 673 K followed by H_2 reduction at 573 K. For HCHO reduction, a 5.0 wt % aqueous HCHO solution with pH being adjusted to 7.0 was added to the suspension containing aqueous $PdCl_2$ solution and the support, and the reduction was carried out at 343 K for 0.5 h with continuous stirring. Then, the product was recovered by filtration followed by washing and drying. Other reductants such as ethanol, glycol, and hydrazine were also used for the preparation of Pd/graphite catalysts. The prepared catalysts were characterized by XRD, N_2-sorption, and TEM. Catalytic reactions were performed at atmospheric pressure and 283 K in a glass reactor. H_2 and O_2 were added via a glass frit to a stirred slurry containing the acidified solvent and the catalyst. H_2 conversion was analyzed by on-line gas chromatography, and the concentration of H_2O_2 was measured with colorimetry after complexation with a $TiOSO_4/H_2SO_4$ reagent.

Table 1. Catalytic performances of supported Pd catalysts (Pd content, 2.5 wt %) for H_2O_2 synthesis from H_2 and O_2[a]

Catalyst	H_2O_2 conc. /wt %	H_2 conv. /%	Select. /%
Pd/SiO_2-imp	0.49	19	26
Pd/Na-ZSM-5-imp	0.05	5.8	8.6
Pd/MCM-41-imp	0.40	34	12
Pd/SBA-15-imp	0.39	15	17
Pd/AC-imp	0.03	13	2.4
Pd/graphite-imp	0.51	16	31
Pd/CNT-imp	0.36	32	11
Pd/charcoal-imp	0.26	14	18
Pd/SiO_2-HCHO-red	0.47	22	21
Pd/AC-HCHO-red	0.11	5.6	20
Pd/graphite-HCHO-red	0.95	17	55
Pd/CNT-HCHO-red	0.43	21	21
Pd/charcoal-HCHO-red	0.48	10	47

[a]Reaction conditions: $T = 283$ K; $H_2/O_2 = 1/4$ (N_2, 16.7%); $F = 60$ mL min^{-1}; $W = 0.050$ g; solvent: aqueous ethanol solution (83%), HCl 0.17 mol dm^{-3}; reaction time, 4 h.

Table 1 shows the catalytic performances of supported Pd catalysts prepared by either impregnation (denoted as imp) or HCHO reduction (denoted as HCHO-red). Among the supports examined in this work, graphite was found to be the most effective one for H_2O_2 formation. Especially, for the series of catalysts prepared by HCHO reduction, Pd/graphite exhibited outstanding H_2O_2 formation activity and selectivity. As far as we know, the superiority of graphite in H_2O_2 direct synthesis has not been reported so far in scientific journals. As compared with other carbon materials, graphite possessed a very lower surface area but much higher conductivity (Table S1 in the Supporting Information).[7] The higher conductivity may contribute to the higher H_2O_2 formation activity and selectivity.

We have investigated the effect of Pd content on catalytic performances of Pd/graphite catalysts prepared by both impregnation and HCHO reduction. The results in Figure 1 further confirm that the catalysts prepared by HCHO reduction are significantly better than those prepared by conventional impregnation for H_2O_2 direct synthesis. For the series of catalysts prepared by HCHO reduction, H_2 conversion, H_2O_2 formation activity and selectivity first increased with increasing Pd content and

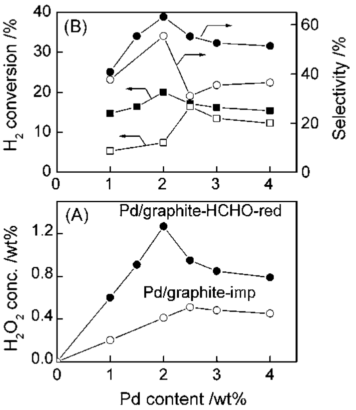


Figure 1. Effect of Pd content on catalytic performances of Pd/graphite catalysts prepared by impregnation and HCHO reduction. Reaction conditions: $T = 283\,\mathrm{K}$; $H_2/O_2 = 1/4$ (N_2, 16.7%); $F = 60\,\mathrm{mL\,min^{-1}}$; $W = 0.050\,\mathrm{g}$; solvent: aqueous ethanol solution (83%), HCl $0.17\,\mathrm{mol\,dm^{-3}}$; reaction time, 4 h. White and black symbols are for the Pd/graphite-imp and Pd/graphite-HCHO-red, respectively.

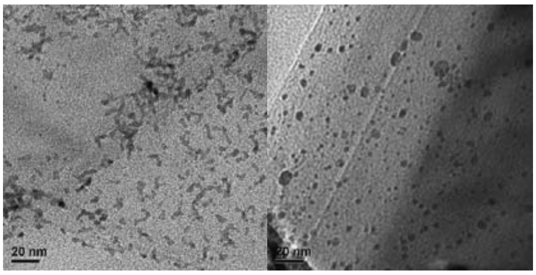
then reached maxima at a Pd content of 2.0 wt %. Further increases in Pd content decreased both the activity and the selectivity. Over the 2.0 wt % Pd/graphite-HCHO-red catalyst, the selectivity for H_2O_2 formation reached 63%, and a H_2O_2 concentration of 1.3 wt % was obtained after 4 h of reaction.

The time course over the 2.0 wt % Pd/graphite-HCHO-red catalyst shows that the concentration of H_2O_2 increases almost proportionally to reaction time (Figure S1 in the Supporting Information),[7] indicating that the catalyst is stable and the secondary reactions are not serious. The selectivity for H_2O_2 formation changes only slightly with reaction time, and is kept at >60%. We have checked the leaching of Pd from the solid catalyst by ICP analysis, and the result reveals that the loss of Pd from the 2.0 wt % Pd/graphite-HCHO-red is less than 5% after 4 h reaction, which is significantly lower than that from the Pd/SiO_2 catalyst.[6] In addition, the introduction of the H_2/O_2 gas mixture into the separated liquid phase after reaction without solid catalyst did not result in H_2O_2 formation.

Further studies with the 2.0 wt % Pd/graphite-HCHO-red catalyst showed that the presence of HCl enhanced the activity and selectivity for H_2O_2 formation, and the formation of H_2O_2 increased with the concentration of HCl (Figure S2 in the Supporting Information).[7] Moreover, we have clarified that the present catalyst could also work efficiently by using other acids such as H_2SO_4, HNO_3, and H_3PO_4 or using other solvents such as CH_3OH, CH_3CN, and isopropanol.

TEM observations reveal that the morphologies of Pd/graphite catalysts prepared by different methods are quite different (Figure 2). Over the Pd/graphite-HCHO-red sample, we mainly observed worm-like Pd nanoparticles, and the diameters were mostly 2–4 nm (mean diameter, 3.3 nm). On the other hand, spheric Pd nanoparticles with sizes of 2–14 nm (mean size, 5.1 nm) were observed over the Pd/graphite-imp sample. It is reasonable to speculate that the size and morphology of Pd nanoparticles may play roles in H_2O_2 selective formation.

Pd/graphite catalysts prepared by chemical reductions with other reductants including ethanol, glycol, and hydrazine have also been examined for H_2O_2 direct synthesis. It is of interest to note that the catalysts prepared by ethanol and glycol reductions also contain Pd with worm-like morphology and exhibit higher H_2O_2 formation activity and selectivity, whereas the catalyst prepared by hydrazine reduction contains larger Pd particles and shows very poor catalytic performances (Table 2).



(a) (b)

Figure 2. TEM images of 2.0 wt % Pd/graphite catalysts prepared by HCHO reduction (a) and impregnation (b).

Table 2. Catalytic performances of 2.5 wt % Pd/graphite catalysts prepared by using different reductants[a]

Reductant	H_2O_2 conc. /wt %	H_2 conv. /%	Select. /%	Pd morph. (size/nm)
HCHO	0.95	17	55	Worm-like (3.3)
Ethanol	0.84	15	55	Worm-like (4.2)
Glycol	0.85	16	55	Worm-like (4.8)
Hydrazine	0.10	15	7.0	Spheric (21)

[a]Reaction conditions are the same as in Table 1.

In conclusion, we have found that Pd/graphite can be an efficient catalyst for the direct synthesis of H_2O_2 from H_2 and O_2. The Pd/graphite catalyst prepared by HCHO reduction exhibits significantly higher H_2O_2 formation activity and selectivity than that prepared by conventional impregnation. The size and morphology of Pd nanoparticles may play roles in H_2O_2 selective formation.

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7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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