Direct Formation of Hydrogen Peroxide with H_2 and O_2 over Anthraquinone Encapsulated Pd-Y Zeolite

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Hydrogen peroxide is known as a green oxidizer and utilized as a mild oxidant in many oxidation reactions.[1] Traditionally, hydrogen peroxide has been commercially produced by the anthraquinone process known as AO process[2] which comprises cyclic hydrogenation and oxidation of alkylanthraquinones in an appropriate working solution. The product hydrogen peroxide is extracted with water from working solution and the corresponding aqueous peroxide solution is possibly contaminated with organics. The hydrogen peroxide should be used for many industrial applications after removal of organics due to environmental issues. Those are the main reason why the AO process is characterized as being complex and capital intensive.

Recent efforts are concentrated on the direct synthesis of H_2O_2 with H_2 and O_2 over heterogeneous catalysts[3,4] and by photochemical processes.[5] Du Pont[6] has disclosed the catalytic production of H_2O_2 by hydrogen oxidation over a supported palladium catalyst in an aqueous solution. While these materials show high activity with 85% selectivity and 14% conversion, it requires high pressures of hydrogen and oxygen to prepare useful concentrations of hydrogen peroxide. There are many other problems such as low concentrations of product, low selectivity (thus high hydrogen consumption), low reaction rates, and high acid content.

The processes which do not require organic solvents for direct conversion of hydrogen and oxygen to hydrogen peroxide has yet to be developed due to the environmental and economic considerations.

Herron and Tolman[7] have first demonstrated the nature mimicking system by using zeolite catalysts containing Pd(0) and Fe(II), which generate hydrogen peroxide at the palladium sites.

In this study, heterogeneous catalysts for the direct production of hydrogen peroxide from hydrogen and oxygen was designed by the inclusion of 2-ethylanthraquinone (2-EAQ) together with Pd species on Y zeolite through encapsulation. Such encapsulated catalysts can produce H_2O_2 from H_2 and O_2 in aqueous solution and its production is synergistically enhanced with an aid of the encapsulated 2-ethylanthraquinone in faujasite pores.

This encapsulated zeolite catalytic system will lead to active solid catalysts for a wide range of hydrogen peroxide mediated oxidation reaction.[8,9]

2-EAQ/Pd-Y was prepared as follows. Palladium was loaded in the NaY (Si/Al=4, Uetikon) by stirring at 60 °C for 12 h with aqueous Pd(NH$_3$)$_4$Cl$_2$ solution. Zeolite loaded with Pd(NH$_3$)$_4$Cl$_2$ was then calcined by heating in air at 550 °C

for 6 h. Reduction of this sample with H_2 at 300 °C for 12 h gave the supported palladium metal over NaY. 3 g of dehydrated Pd-Y was stirred at 60 for 3 days using 0.1M 2-EAQ in 50 mL benzene. Then the sample was filtered and washed with benzene and acetone until no 2-EAQ was detected in the filterate. 2-EAQ loading was determined by CHN elemental analysis and the concentration of Pd was analyzed by ICP method. FT-IR spectra were recorded on a Nicolet Magna-IR 560 spectrometer over the range of 1200-4000 cm^{-1}. XRD was carried out on a Rigaku diffractometer using monochromatized Cu K$_\alpha$ radiation.

Catalytic reaction was performed at room temperature by bubbling 50 vol. % H_2 in N_2 and 50 vol. % O_2 in N_2 simultaneously into 0.01 N HCl solution containing 0.1 g catalyst. The concentration of H_2O_2 accumulated was determined by the titration with a standard potassium permanganate solution.

XRD pattern of 2-EAQ/Pd-Y shows no structural change compared with Pd-Y or Na-Y. The encapsulated catalyst contains 1.8 wt% 2-EAQ which implies that there is approximately one 2-EAQ molecule in two supercages of Y zeolite. Encapsulated sample was characterized by FT-IR spectroscopy and thermogravimetric analysis. There are no significant bands in the region of 1200-2000 cm^{-1} for Pd-Y, however, 2-EAQ/Pd-Y and 2-EAQ show similar spectra in this region indicating that 2-EAQ is encapsulated over Pd-Y. Absorption bands of 2-EAQ/Pd-Y are shifted to the lower energy direction by about 5-10 cm^{-1} compared to those of 2-EAQ. According to TG analysis, 2-EAQ encapsulated in 2-EAQ/Pd-Y and 2-EAQ itself are decomposed at 283 and 366 °C, respectively. The comparative catalytic activities of H_2O_2 generation were investigated by simultaneous feeding both H_2 and O_2 over 2-EAQ-Y, Pd-Y and 2-EAQ/Pd-Y, respectively. As shown in Table 1, H_2O_2 generation over 2-EAQ/Pd-Y is about 2 and 6 times higher than that of Pd-Y

Table 1. Direct formation of H_2O_2 by H_2 and O_2 over encapsulated Y zeolites

Catalysts	loadings (wt.%)	[H_2O_2] (mmole)
NaY	-	0
2-EAQ-Y	2-EAQ=1.8	0.6
Pd-Y	Pd=1.0	2.4
2-EAQ/Pd-Y	Pd=1.0 2-EAQ=1.8	4.0

Reaction conditions: catalyst 0.1 g, 0.01 N HCl 400 mL, H_2=O_2=40 mL/min., temp.=28 °C, 1 h.
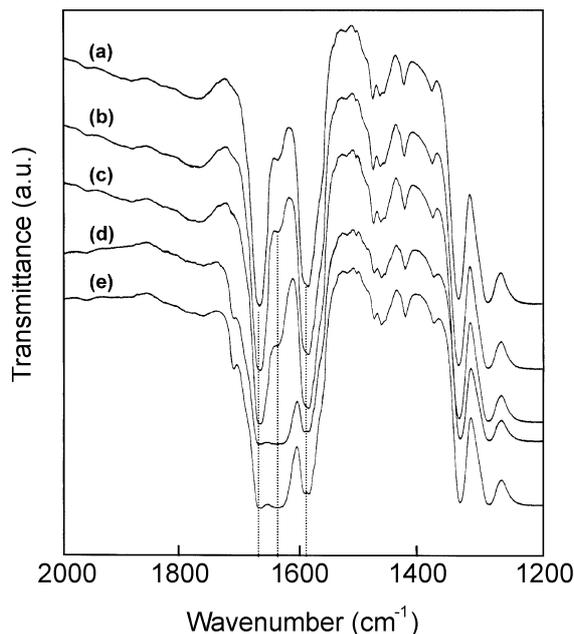
Figure 1. FT-IR spectra of 2-EAQ-Y after (a) evacuation at 200 °C for 2 h, (b) adsorption of 10 torr of H_2 at RT for 20 min, (c) adsorption of 10 torr of O_2 at RT for 20 min., (d) heating at 60 °C for 10 min., and (e) evacuation at room temperature.

Figure 2. FT-IR spectra of 2-EAQ/Pd-Y after (a) evacuation at 200 °C for 2 h, (b) adsorption of 10 torr of H_2 at RT for 20 min., and (c) adsorption of 10 torr of O_2 at RT for 20 min.

and 2-EAQ-Y, respectively. Since the Pd loading is important for the generation of H_2O_2, the catalytic reactions were carried out over 2-EAQ/Pd-Y with different Pd loadings in the range of 0.3-2.0 wt.%. The highest 4 mmoles of H_2O_2 is produced over 2-EAQ/Pd-Y with 1.0 wt.% of Pd. The generation of H_2O_2 over 2-EAQ/Pd-Y was also studied as a function of feed ratio of H_2 to O_2, resulting that the highest production is obtained when the ratio of H_2/O_2 is 1. Catalytic activity for the production of H_2O_2 increases up to the maximum reach at 1 h, beyond which it declines slowly with time. After 3 h, the production amount of H_2O_2 decreases by about 15% compare to the maximum value. It is unclear but reduction of catalytic activity is probably due to the extraction of 2-EAQ from the zeolite during the reaction. This is the first example that H_2O_2 can be produced directly from H_2 and O_2 over 2-EAQ/Pd-Y as a catalyst for activating hydrogen and oxygen in aqueous system.

When 2-EAQ/NaY sample was evacuated at 200 °C for 2 h, several characteristic bands of 2-EAQ were observed at 1670, 1589, 1337, 1286 cm^{-1} as shown in Figure 1. The former two bands are due to -C=O group and the latter two bands to -CH group of 2-EAQ.[10] Upon adsorption of 10 torr of H_2 at room temperature for 1 h, there is no significant change on FT-IR spectrum. Upon contacting 10 torr O_2 at room temperature for 1 h, subsequently, the band intensities at 1670 and 1589 cm^{-1} were reduced slightly. On the other hand, significant change is observed after heating the sample at 60 °C for 30 min. Bands at 1670, 1589 cm^{-1} become broader and smaller, while broad band centered at 1640 cm^{-1} increases gradually, which might indicate that carbonyl group in 2-EAQ hydrogenates slowly, being changed from -C=O to -COH. And a new small band at 1780 cm^{-1} appears
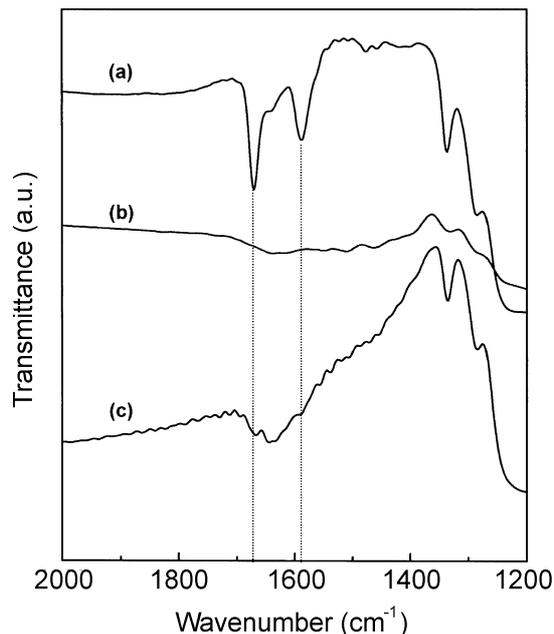
which is not identified clearly yet. During this experiment, there is no change for bands at 1337, 1286 cm^{-1}. Finally, upon evacuation at 200 °C for 1 h, FT-IR spectrum becomes identical to Figure 1(a), which is probably due to that formed H_2O_2 has disappeared upon evacuation. 2-EAQ-Y seems to behave like 2-EAQ in non-aqueous solution system as far as production of H_2O_2 concerned. Faujasite cavity of Y zeolite could play a role as a solvent, and encapsulated 2-EAQ could enable the dissociation of H_2 into a loosely bound hydrogen atoms close to the encapulated 2-EAQ in faujasite.

When Pd/Na-Y was dehydrated at 200 °C for 2 h, there appears a broad small band at 1640 cm^{-1}. After subsequent addition of 9 torr of H_2 and O_2, respectively, on the dehydrated Pd/NaY, a band at 1640 cm^{-1} is enhanced remarkably by about 5 times, whose FT-IR spectrum becomes identical to that of the dehydrated Pd-Y after evacuation at 200 °C for 3 h. It seems that Pd easily adsorb hydrogen, and forms palladium hydride. Then -OH containing compound such as H_2O_2 or H_2O might be formed readily upon contacting O_2 over palladium hydride. It is known that H_2O_2 can be produced easily over Pd-supported catalyst by H_2 and O_2.[2,6]

Although there is no direct evidence for the reaction mechanism on the generation of H_2O_2 with H_2 and O_2 over encapsulated solid catalyst, according to the results of Santacesaria *et al.*,[11] possible reaction mechanism is proposed as follows. When 2-EAQ/Pd-Y was evacuated at 200 °C under < 10^{-5} torr, -C=O stretching bands at 1669 and 1584 cm^{-1}, -CH asymmetric and symmetric bending bands at 1332 and 1281 cm^{-1}, respectively, of 2-EAQ are observed. Upon contacting 10 torr of H_2 on this catalyst for 10 min at room temperature, -C=O band of 2-EAQ is disappeared. On the other hand, no change was observed for -CH bands. When H_2 adsorbed sample was evacuated followed by contacting 10

torr of O_2, -C=O bands at 1669, 1584 cm^{-1} are appeared again, and simultaneously new broad bands at 3200-3500 cm^{-1} and 1635 cm^{-1} are observed. This result implies that 2-EAH$_2$Q has converted into 2-EAQ reversibly and -OH containing compounds such as H_2O_2 or H_2O are produced at the same time. The reason for disappearing of -C=O band seems to be due to that -C=O was changed into -COH by H_2 which was activated by metallic Pd, indicating that 2-EAQ is converted into 2-EAH$_2$Q (2-ethylanthrahydroquinone).

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