Hydrogen peroxide is known as a green oxidizer and utilized as a mild oxidant in many oxidation reactions. Traditionally, hydrogen peroxide has been commercially produced by the anthraquinone process known as AO process 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 \( H_2 O_2 \) with \( H_2 \) and \( O_2 \) over heterogeneous catalysts and by photochemical processes. Du Pont has disclosed the catalytic production of \( H_2 O_2 \) 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.

Table 1: Direct formation of \( H_2 O_2 \) by \( H_2 \) and \( O_2 \) over encapsulated Y zeolites

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>loadings (wt.%)</th>
<th>([H_2 O_2]) (mmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>2-EAQ-Y</td>
<td>2-EAQ=1.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Pd-Y</td>
<td>Pd=1.0</td>
<td>2.4</td>
</tr>
<tr>
<td>2-EAQ/Pd-Y</td>
<td>Pd=1.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>2-EAQ=1.8</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: catalyst 0.1 g, 0.01 N HCl 400 mL, \( H_2=O_2=40 \) mL/min., temp.=28 °C, 1 h.
and 2-EAQ-Y, respectively. Since the Pd loading is important for the generation of H₂O₂, 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 H₂O₂ is produced over 2-EAQ/Pd-Y with 1.0 wt.% of Pd. The generation of H₂O₂ over 2-EAQ/Pd-Y was also studied as a function of feed ratio of H₂ to O₂, resulting that the highest production is obtained when the ratio of H₂/O₂ is 1. Catalytic activity for the production of H₂O₂ increases up to the maximum reach at 1 h, beyond which it declines slowly with time. After 3 h, the production amount of H₂O₂ decreases by about 15% compared 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 H₂O₂ can be produced directly from H₂ and O₂ 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. Upon adsorption of 10 torr of H₂ at room temperature for 1 h, there is no significant change on FT-IR spectrum. Upon contacting 10 torr O₂ 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 H₂O₂ has disappeared upon evacuation. 2-EAQ-Y seems to behave like 2-EAQ in non-aqueous solution system as far as production of H₂O₂ concerned. Faujasite cavity of Y zeolite could play a role as a solvent, and encapsulated 2-EAQ could enable the dissociation of H₂ into a loosely bound hydrogen atoms close to the encapsulated 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 H₂ and O₂, 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 H₂O₂ or H₂O might be formed readily upon contacting O₂ over palladium hydride. It is known that H₂O₂ can be produced easily over Pd-supported catalyst by H₂ and O₂.

Although there is no direct evidence for the reaction mechanism on the generation of H₂O₂ with H₂ and O₂ over encapsulated solid catalyst, according to the results of Santacesaria et al., possible reaction mechanism is proposed as follows. When 2-EAQ/Pd-Y was evacuated at 200 °C under < 10⁻³ 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 H₂ 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 H₂ adsorbed sample was evacuated followed by contacting 10

![Figure 1](image1.png)  
Figure 1. FT-IR spectra of 2-EAQ-Y after (a) evacuation at 200 °C for 2 h, (b) adsorption of 10 torr of H₂ at RT for 20 min., (c) adsorption of 10 torr of O₂ at RT for 20 min., (d) heating at 60 °C for 10 min., and (e) evacuation at room temperature.

![Figure 2](image2.png)  
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 H₂ at RT for 20 min., and (c) adsorption of 10 torr of O₂ at RT for 20 min.
torr of O₂, -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-EAH₂Q has converted into 2-EAQ reversibly and -OH containing compounds such as H₂O₂ or H₂O 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 H₂ which was activated by metallic Pd, indicating that 2-EAQ is converted into 2-EAH₂Q (2-ethylanthrahydroquinone).

References