Study on the new hydrogenation catalyst and processes for hydrogen peroxide through anthraquinone route

Hui Shang a,*, Hongjun Zhou a,**, Zehua Zhu b, Wenhui Zhang a

a State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, PR China
b SINOPEC CORP. Research Institute of Petroleum Processing, Beijing 100083, PR China

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A B S T R A C T
The main process for industrial synthesis of hydrogen peroxide is to subject 2-ethylanthraquinone to cyclic hydrogenation and oxidation. Hydrogenation catalyst is one of the key techniques of anthraquinone route. A new egg-shell palladium catalyst with racshig-ring alumina supported was developed for meeting the mechanism and improving mass transformation based on the kinetics and mass transfer theory, the effects of materials feeding methods together with operating conditions on the hydrogenation efficiency were detailed. It was concluded that the egg-shell palladium catalyst developed by this research has higher hydrogenation efficiency than the commercial contrast catalysts.

1. Introduction

Hydrogen peroxide (H₂O₂) is an important green chemical product because its utilization does not cause any secondary pollution. It is widely used in the military industry, textile industry, papermaking, chemical synthesis, environmental protection, food processing, medical sterilization and other fields.

H₂O₂ is commercially produced using the anthraquinone process [1–3], where 2-ethylanthraquinone (eAQ) in an organic solvent is first hydrogenated in the presence of a supported Pd catalyst to yield 2-ethylanthrahydroquinone (eAQH₂) under mild reaction conditions (temperature 40–80 °C, pressure: 0.3 to several Mpa). The eAQH₂ is then oxidized by molecular oxygen to produce hydrogen peroxide regenerating eAQ in the process at the temperature of 40–60 °C. Fig. 1 details the reactions.

The reactions for H₂eAQ are similar, with hydrogenation to H₂eAQH₂ first and then oxidized to H₂eAQ with a molecule of H₂O₂ production simultaneously.

In working solution, eAQH₂, eAQ and H₂O₂ are produced and separated subsequently via water extraction. The H₂O₂ is evaporated and distilled to produce final hydrogen peroxide products (27.5–70% in concentration) [4]. The working solution from the extraction tower is purified by alkali and treated in a post-treatment step. Subsequently it is circulated back to the hydrogenation reactor. Therefore, the working solution contains active AQs, organic solvent as well as by-products formed during the hydrogenated and oxidized step.

The regenerated eAQ is again hydrogenated in the next cycle to obtain another molecule of H₂O₂. Although starting with eAQ the main reaction is as shown above, some eAQH₂ on further hydrogenation is converted to tetrahydro-2 ethylanthrahydroquinone (H₄eAQH₂). When H₄eAQH₂ is oxidized it produces one molecule of H₂O₂ and one molecule of tetrahydroanthraquinone (H₄eAQ). Like eAQ, this H₄eAQ is also used again and again to produce H₂O₂. During the circulation, eAQ and H₂eAQH₂ can also be degraded by deep hydrogenation of aromatic ring, the hydrolysis of carbonyl group in inactive AQs, and further deep oxidation into by-products, which lose the ability to generate H₂O₂.

Santacesaria et al. reported that hydrogenation of anthraquinone derivatives on Pd catalyst is a fast reaction, and mass transfer resistance controls the reaction rate in conventional reactors [5].

The hydrogenation reaction was proved to be a zero-order kinetics for hydrogen, and an first order kinetic law for eAQ and H₄eAQ [5–8]. Studies by Drelinkiewicz and Waksmundzka [9] used Pd/Si–Al (Pd 2%) revealed that the activation energy was as low as 12.5–20.9 kJ/mol with the catalyst’s diameter of 0.06–0.2 mm and the activation energy of 29.3–33.5 kJ/mol with the catalyst’s diameter less than 0.06, indicating that the former tests were influenced by internal diffusion, whilst the latter tests with smaller catalyst particles eliminated such influence.
The activity and selectivity of hydrogenation catalyst determine the device productive capacity. Side reactions can also be avoided by improving the catalyst's high activity and selectivity. Based on research results and plant operation experience, a catalyst with a high surface area and a structure conducive to reactant's diffusion in the bed as well as a process to the benefit of external diffusion are required, both of which are the technology development trend in anthraquinone hydrogenation.

This paper discusses the most important issues encountered during the development of industrial AQ process with the focus on the key step – hydrogenation of active anthraquinones. An innovative catalyst was developed according to the hydrogenation kinetics within this research and its performance was investigated.

2. Experimental

The hydrogenation of working solution in a trickle bed reactor containing very small particles of Pd/Al2O3 catalyst was investigated in this paper. The working solution was a mixture of eAQ, H4eAQ, trioctyl phosphate and aromatics of C9–C10, there contained 22.1 g/L eAQ and 116.5 g/L H4eAQ, the volume ratio of C9–C10 aromatics to trioctyl phosphate is 3:1. The characteristics of the working solution at 50 °C are: density: 897.76 kg/m³, surface tension: 0.349 N/s, viscosity: 1.0237 × 10⁻³ Pa s.

2.1. Catalyst’s preparation

Raschig ring alumina was selected as a support with a size of φ3 × φ2 × 5 (mm), the support was impregnated with PdCl2 solution in a pH value of 3–4, after 2 h the sample was washed with water only until Cl⁻ ions were removed and then dried at room temperature. The prepared catalyst named as GXH–1 was dried for 16 h at 105 °C in an oven and calcined at 550 °C in a furnace, whose properties are shown in Table 1.

2.2. Hydrogenation experiments and analytical procedure

The activity test was carried out in a stainless steel reactor with an internal diameter of 50 mm and height of 620 mm. The experimental setup is schematically shown in Fig. 2.

The catalyst was reduced by hydrogen at a temperature of 60 °C and a pressure of 0.2 MPa for 12 h in the reactor, and then cooled down to a desired temperature. The reactor was first flushed by aromatics and then packed by 510 g GXH–1 catalyst with the height of 600 mm. Nitrogen was used for pressure and leakage tests. Hydrogen gas employed in this study was obtained from a gas cylinder with an ultra high purity grade (99.999%). The eAQ solution was pumped at a pre-determined flow rate. Hydrogen gas flowed from a cylinder through a flow meter. The hydrogen and working solution were mixed in the mixer and then downstream or upstream into the reactor packed with GXH–1 catalyst. The product mixture was collected and the un-reacted hydrogen was vented to the atmosphere. The liquid product was collected for analysis.

Hydrogenation efficiency was defined as the grams of hydro peroxide produced by 1 L working solution.

3. Results and discussion

3.1. GXH–1’s hydrogenation efficiency

The performances of GXH–1 catalyst together with two commercial catalysts used in China for hydrogen peroxide
production were investigated at temperature of 40–100 °C, pressure of 0.2 MPa, hydrogen space rate of 600 h⁻¹, and liquid space rate of 12 h⁻¹. Results are shown in Fig. 3. Fig. 3 shows that the activities of GXH-1 are much higher than the other two commercial used catalysts through the temperature range of 40–100 °C. A and B are industrial catalysts used for contrast agents in this research, which are used in Yueyang petrochemical plant, their operating conditions are as the followings: temperature of 40–75 °C, pressure of 0.1–0.35 MPa, and the LHSV of 7–12 h⁻¹.
Intrinsic kinetics for the hydrogenation of eAQ and H₂eAQ are very important toward the development of AO process, and it was reported by a few papers that the hydrogenation reaction rate is first order with respect to hydrogen partial pressure and zero order with respect to eAQ and H₂eAQ concentration [10,11]. Therefore eAQ and H₂eAQ can be taken as one single substance due to the identical hydrogenation kinetics. The reaction rate constant for the hydrogenation of eAQ in a stirring slurry reactor excluding any mass transfer resistance are shown in Eq. (1) [12], and eAQ’s production rate can be written as Eq. (2):

$$K_{eAQ} = K_{eAQ}^0 \exp(-E_{AQ}/RT)$$  \hspace{1cm} (1)$$

$$R_{eAQ} = -\frac{dC_{eAQ}}{dt} = \eta m_p K_{eAQ} P_{H_2}$$  \hspace{1cm} (2)$$

The hydrogenation process is thought to act at isothermal temperature due to no obvious thermal effect of eAQ hydrogenation. The reactant’s gas and liquid mass balance and momentum balance can be calculated using axial dispersion model based on the two-film theory, and the axial dispersion reactor model is thus achieved as the followings [13,14].

**Mass balance:**

**Gas phase:**

$$D_{H_2} \frac{d^2 C_{H_2}}{dt^2} - u_{0g} \frac{dC_{H_2}}{dt} - N_{H_2} = 0$$  \hspace{1cm} (3)$$

**Liquid phase:**

$$D_{H_2} \frac{d^2 C_{H_2}}{dt^2} - u_{0l} \frac{dC_{H_2}}{dt} + N_{H_2} - N_{H_2} = 0$$  \hspace{1cm} (4)$$

$$D_{eAQ} \frac{d^2 C_{eAQ}}{dt^2} - u_{0l} \frac{dC_{eAQ}}{dt} - N_{eAQ} = 0$$  \hspace{1cm} (5)$$

**Solid phase:**

$$N_{H_2} = N_{eAQ} = R_{eAQ}$$  \hspace{1cm} (6)$$

**Momentum balance:**

$$\frac{d\rho}{dt} = -\frac{\Delta \rho}{\Delta t}_{lg}$$  \hspace{1cm} (7)$$

Total effective factor $\eta$ will be achieved using Ramachandran and Chaudhari’s method [7]. If the reaction is totally controlled by external dispersion, then:

$$N_{H_2} = k_s \theta_i [C_{H_2} - C_{H_2}^\theta]$$  \hspace{1cm} (8)$$

$$N_{H_2} = k_1 \theta_i [C_{H_2}^\theta - C_{H_2}]$$  \hspace{1cm} (9)$$

$$N_{H_2} = k_s \theta_i [C_{H_2} - C_{H_2}^\theta]$$  \hspace{1cm} (10)$$

When the gas–liquid mixture reaches their balance at the phase interface, following equation can be obtained according to Henry’s law:

$$C_{H_2} = H C_{H_2}$$  \hspace{1cm} (11)$$

From literature, eAQ and H₂eAQ’s hydrogenation reaction rates are in first order, the reaction rate can be written as (12) when internal dispersion is considered:

$$R_{eAQ} = -\frac{dC_{eAQ}}{dt} = \eta m_p K_{eAQ} C_{H_2}$$  \hspace{1cm} (12)$$

According to the intrinsic reaction kinetics, (2) = (12), then:

$$K_{eAQ} C_{H_2} = K_{eAQ} P_{H_2}$$  \hspace{1cm} (13)$$

Taken hydrogen acting as ideal gas and there is no external dispersion resistance, the hydrogen concentration at catalyst surface and eAQ’s reaction rate constant can be written as Eqs. (14) and (15).

$$C_{H_2} = \frac{P_{H_2}}{RT}$$  \hspace{1cm} (14)$$

$$K_{eAQ} = K_{eAQ} RT$$  \hspace{1cm} (15)$$

The reactions’ rate should be equal for each step once the process reaches their steady-state, Eqs. (8)–(12) can be combined and the following equations would be obtained:

$$R_{eAQ} = -\frac{dC_{eAQ}}{dt} = K_0 C_{H_2}$$  \hspace{1cm} (16)$$

$$\frac{1}{K_0 \theta_i} = \frac{1}{K_0 \theta_i} + H K_0 \theta_i$$  \hspace{1cm} (17)$$

According to Eqs. (15) and (17):

$$K_0 = \frac{1}{K_0 \theta_i} + \frac{H}{K_0 \theta_i} + \frac{H}{K_0 \theta_i}$$  \hspace{1cm} (18)$$

$K_0$ is the macroreaction rate constant, whose reciprocal is the process resistance. From Eq. (18), the process resistance is composed by five parts, four of which are mass transfer resistance, and the other one is chemical reaction resistance.

$1/\kappa_s \theta_i$ is the gas-film resistance, $H/\kappa_s \theta_i$ is the liquid-film resistance, $H/\kappa_s \theta_i$ is the liquid-film resistance at liquid–solid interface, $H/\eta m_p K_{eAQ} RT$ is the chemical resistance and internal dispersion resistance.

From the view of new catalyst’s development, the chemical resistance’s contribution from Eq. (18) is really important. The racshig-ring egg-shell catalyst can reduce the internal diffusion resistance to a great extent, due to the significant small catalyst particles, especially when the particle size reduces to microflake which covers on the surface of the support, the Pd’s penetration depth is only 0.2 mm for GXH-1.

Catalyst’s effective coefficient can be achieved by (19) for the spherical particles, (20) for flat flake particles and (21) for long cylinder particles:

$$\eta = \left( \frac{1}{\tanh(3\theta)} - \frac{1}{3\theta} \right)$$  \hspace{1cm} (19)$$

**Fig. 3.** Comparison of catalysts’ activity.
Several origins originated the coefficient. The coefficient 30–40% can fully contribute to effective catalysts.

\[ f = \text{tanh} \frac{e}{A} \]

From large pores, GXH-1, Raschig contact, the hydrogenation efficiency of GXH-1 catalysts; it is certified that GXH-1 catalyst developed by this work can efficiently reduce the internal diffusion resistance.

\[ \phi = \frac{V_{eq}}{A_{b}} \left( \frac{K_{eq}}{D_{eq}} \right) \]

\[ \eta = \frac{1}{\phi} \left( 2 \phi \right) \]

\[ \phi \] is the Thiele Module, which is defined as: \( \phi = \frac{V_{eq}/A_{b}}{K_{eq}/D_{eq}} \), the value of \( V_{eq}/A_{b} \) represents the equivalent length of catalyst particle. For different particle shapes, the value of \( V_{eq}/A_{b} \) is different, for example, for flat plates, the value is half thickness; for cylinder with ends sealed and sphere, the value is the radius, whilst for long cylinder, the value is half radius.

The effective coefficient (\( \eta \)) for these three shape catalysts can be found in Table 2 [15].

If taken the four-leaf clover catalyst as the cylinder, and the Raschig ring as the flat-plate particle. Table 2 clearly shows that the shape of flat-plate contributes to higher \( \eta \) than cylinder and sphere catalysts; it is certified that GXH-1 catalyst developed by this work can efficiently reduce the internal diffusion resistance.

Due to the fact that the internal diffusion resistance is mainly originated by particle pore distribution, the pore size distribution of catalysts A, B and GXH-1 were analyzed through BET. Fig. 4 illustrates the pore size distributions based on BET desorption data. From Fig. 4 and other BET results, most of the pores in catalyst A have smaller diameter than those in catalysts B and GXH-1, since large pore helps to reduce the mass transfer resistance.

Although catalyst B has the similar pore size distribution to GXH-1, based on the Fick Law [16], the effective diffusion coefficient \( D_{eq} \) can be expressed as (22):

\[ D_{eq} = \frac{e}{\tau} D_{b} \]

From Table 1 catalyst GXH-1 has higher voidage than the other two commercial catalysts, resulting higher effective diffusion coefficient. Furthermore, the raschig ring catalyst particle has an internal and external surface, which can significantly enhance the contact surface area for chemical reactions, thus reduce the external diffusion.

From the above discussions, together with Table 1, GXH-1 has several significant advantages over the other two commercial catalysts: 20% higher in surface area, about 30% higher in porosity, 30–40% lighter in bulk density, and the Pd penetration depth was smaller than the commercial catalyst, making its corresponding hydrogenation efficiency better and competitive in industrializing the AO process.

### 3.2. Effects of operating parameters on the hydrogenation efficiency

Material feeding method such as gas–liquid up-flow and down-flow would influence the materials residence time in the reactor and thus affect the reaction. Downstream of working solution and hydrogen and upstream together with operating conditions were fully investigated in this section. Two different concentrations working solution of active anthraquinones were employed for this research, both of which were sampled from the industry equipment sideline. One named No. 1 working solution has \( eAQ \) of 239.6 mol/m³ and \( H_{2}eAQ \) 366.7 mol/m³, the other named No. 2 consists \( eAQ \) of 93.4 mol/m³ and \( H_{2}eAQ \) of 484.9 mol/m³.

#### 3.2.1. Effects of temperature on the hydrogenation efficiency

Influence of temperature together with feeding method on GXH-1 hydrogenation efficiency is shown in Fig. 5, the experiments were carried out with hydrogen pressure of 0.2 MPa, LHSV of 15 L/h and hydrogen flow rate of 120 L/h.

Fig. 5 indicates that the hydrogenation efficiency increases with temperature increment for both No. 1 and No. 2 solutions, especially at above 80 °C. The influence of temperature on the hydrogenation efficiency of No.1 sample is higher than that of No. 2, indicating that the hydrogenations of \( eAQ \) and \( H_{2}eAQ \) occur at the same time, only because the active energy of \( H_{2}eAQ \) is lower than \( eAQ \), the conversion at low temperature is higher, whereas, \( eAQ \)'s hydrogenation gives the most contribution at higher temperature. Fig. 4 also clearly indicates that at the same temperature the hydrogenation efficiency from upstream method is significant higher than downstream method.

![Fig. 5. Effects of temperature on the hydrogenation efficiency for down and up stream feeding methods.](image-url)
3.2.2. Effects of pressure on hydrogenation efficiency

The influence of pressure is shown in Fig. 6. Experiments were carried out at a temperature of 60 °C, LHSV of 15 L/h and hydrogen flow rate of 120 L/h using catalyst GXH-1 and No. 2 sample. Fig. 6 shows that hydrogenation efficiency goes higher with the pressure increasing, which is thought due to the fact that high pressure benefits to the gas molecular numbers reduced reaction, therefore the equilibriums shift to the production direction.

3.2.3. Effects of LHSV on the hydrogenation efficiency

The effects of LHSV on the hydrogenation efficiency and output capacity are shown in Fig. 7. The tests were employed at a temperature of 60 °C, pressure of 0.4 MPa, and hydrogen flow rate of 2 L/min. It can be seen from Fig. 7 that the hydrogenation efficiency slightly decreases with LHSV increasing, which means that the contact time may be not enough for eAQ's hydrogenation.

Both Figs. 5 and 6 clearly show that at the same temperature the hydrogenation efficiency from upstream method is significant higher than downstream method, which may be complained by the following theory.

Based on Eq. (18), it is obvious that the research to reduce 1/κgαl, H/κsαl and H/κsαs is the key matter.

For downstream process:

The surface area of gas–liquid interface increases with gas and liquid flow rate, a1 is much higher than the catalyst's surface area a0. For trickle area, a1 can be calculated as (23):

$$\frac{a_1}{a_0} = 0.81 \left(\frac{\Delta p}{\Delta T} \frac{E}{\nu a_0}\right)^{1.2}$$  (23)

Mass transfer on the trickle bed is high due to the high surface area of gas–liquid interface, not because of the mass transfer coefficient.

1. Gas-film resistance, 1/κgαl

The gas-film resistance can be ignored if the gas substitutes are composed by pure gas and liquid components and reactant production are of non-volatile materials. Therefore, the gas-film resistance can be neglected by using the high purity grade hydrogen (99.99%).

2. Liquid-film resistance, H/κsαl

Et expresses the energy consumption of liquid:

$$E_t = (D_p/\rho)_l u_0.\ \text{When} \ 0.4 < E_t < 10 \ \text{kg/m}^2\text{s}:$$

$$k_l\alpha_l = 0.0011E_t \frac{D_{H_2}}{2.4 \times 10^{-10}}$$  (24)

$$D_{H_2}$$ is the molecular diffusion coefficient of hydrogen from gas phase to liquid phase. When 5 < E_t < 1000 kg/m² s:

$$k_l\alpha_l = 0.017E_t^{0.5}$$  (25)

From (24) and (25) it can be seen that the liquid-film resistance can be efficiently reduced by improving the liquid flow rate and raising bed pressure drop, since upstream process has higher bed pressure drop than downstream process, contributing to reduce the liquid-film resistance.

3. Liquid–film resistance on the liquid–solid interface H/κsαs

The mass transfer coefficient between liquid phase and catalyst’s surface is κsαs, the correlation is:

$$\varepsilon_s h = \frac{0.8}{\Re_t} \Re^{1/2} C_1^{1/3}$$  (26)

When Re_t > 10, the mass transfer coefficient on liquid–solid interface is:

$$sh = 48\Re_t^{1/4}$$  (27)

$$\Re_t = \frac{u_d d_s \rho_l}{\mu_l}, \ \text{Schmidt number} \ \Sc = \frac{\mu_l}{\rho_l D_{H_2}}.$$

Sh = κs/κD is the effective diameter of catalyst particle is d0, $d_0 = d_s/1.5(1 - \varepsilon)$.

From (24)–(27) it can be seen that at the same operating conditions, gas and liquid velocity has more effects on mass transfer in a bubble column.

Further discussion was focused on the reactants' residence time on the catalyst bed for both upstream and downstream. The tests for this propose were conducted on a fixed bed column with the diameter of 80 mm and height of 1585 mm by using water as the mobile phase at 60 °C. The residence time of catalysts A and GXH-1 were investigated, and the results are shown in Fig. 8. It was found that the residence times of upstream process for both GXH-1 and industrial catalyst A are significantly higher than those of downstream process, benefiting to the hydrogenation performance. The experiments also indicate that the residence time from using catalyst GXH-1 is obviously higher than that from A, which is...
thought due to the catalyst’s shape effects. Therefore, according to the above discussions, GXH-1 catalyst developed by this research has excellent hydrogenation performance due to its characteristics.

4. Conclusion

From above sections, the new catalyst GXH-1, developed according to kinetic data and mass transfer model, has higher hydrogenation activity compared to the other two industrial catalysts. Temperature, pressure, LHSV as well as material feeding method have great impact on hydrogenation efficiency. The effect of temperature on hydrogenation efficiency is relative small at the temperature below 80 °C, whereas above 80 °C hydrogenation efficiency increase rapidly with temperature rising. It was also found that the hydrogenation efficiency was enhanced by higher pressure, the materials feeding methods have markedly influenced on the hydrogenation efficiency; up-flow feeding method helps reduce mass transfer resistance, enhancing reactants contact time. At the hydrogen pressure of 0.2 MPa and the same temperature, the hydrogenation efficiency of up-flow process can be enhanced 30% than that of down-flow process.

References