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

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ABSTRACT

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 (H_2O_2) 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.

H_2O_2 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 ($eAQH_2$) under mild reaction conditions (temperature 40–80 °C, pressure: 0.3 to several MPa). The $eAQH_2$ 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 H_4eAQ are similar, with hydrogenation to H_4eAQH_2 first and then oxidized to H_4eAQ with a molecule of H_2O_2 production simultaneously.

In working solution, $eAQH_2$, eAQ and H_2O_2 are produced and separated subsequently via water extraction. The H_2O_2 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 H_2O_2. Although starting with eAQ the main reaction is as shown above, some $eAQH_2$ on further hydrogenation is converted to tetrahydro-2 ethylanthrahydroquinone (H_4eAQH_2). When H_4eAQH_2 is oxidized it produces one molecule of H_2O_2 and one molecule of tetrahydroanthraquinone (H_4eAQ). Like eAQ, this H_4eAQ is also used again and again to produce H_2O_2. During the circulation, eAQ and H_4eAQH_2 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 H_2O_2.

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 H_4eAQ [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.

Abbreviations: AHQ, anthrahydroquinone; AQ, anthraquinones; eAQ, 2-ethylanthraquinone; $eAQH_2$, 2-ethylanthrahydroquinone; H_4EAQ, 2-ethyltetrahydroanthraquinone; H_4EAQH_2, tetrahydro-2-ethylanthrahydroquinone; H_2O_2, hydrogen peroxide; LHSV, liquid hourly space velocity.

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Symbols used

B	hydrogenation efficiency (g/L)
C	concentration (mol/L)
C_{eAQ}	concentration of 2-ethyl-anthraquinone in working solution (mol/L)
C_{eAQ}^0	concentration of 2-ethyl-anthraquinone in working solution (mol/L)
C_{eAQH_2}	mole concentration of anthraquinone in hydrogenation solution (mol/L)
D	diffusion coefficient (m^2/s)
D_b	intrinsic diffusion coefficient (m^2/s)
E	activation energy (kJ/mol)
H	Henry constant of hydrogen (MPa/(cm^3 mol))
I_0	zero-order Bessel function
I_1	first-order Bessel function
k	constant reaction rate (m^3/(s kg))
$k_g a_l$	gas–gas mass transfer coefficient (s^{-1})
$k_l a_l$	gas–liquid mass transfer coefficient (s^{-1})
$k_s a_s$	liquid–solid mass transfer coefficient (s^{-1})
l	reactor bed height (m)
m	mass (g)
m_{Pd}	Pd mass (g)
N	mass transfer rate (kmol/(m^2 s))
P	pressure (MPa)
R	constant, $R = 8.314$ J/(mol K) (J/(mol K))
R_{eAQH_2}	eAQH$_2$'s production rate (mol/(gPd L min))
r	micro-chemical reaction rate (mol/(m^3 s))
s'	selectivity
T	temperature (°C)
t	reaction time (s)
V	consumed volume of potassium permanganate by titration (mL)
V_p	particle volume (m^3)
A_p	particle external surface area (m^2)
ε	the voidage of catalyst bed
η	effective factor
φ	Thiele modulus
τ	Tortuosity factor

Subscripts

H_2	hydrogen
g	gas phase
l	liquid phase
s	solid phase

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 conductive 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.

Table 1
Characteristics of catalysts GXH-1, industrial contrast agents A and B.

Catalyst	A	B	GXH-1
Shape	Sphere	Four-leaf clover	Raschig ring
Pd (%)	0.30 ± 0.02	0.30 ± 0.02	0.28 ± 0.02
Active layer's structure	Egg-shell	–	Egg-shell
Pd penetration (mm)	0.3	0.3	0.2
Bulk density (kg/m^3)	0.78	0.76	0.51
BET surface area (m^2/g)	100	99	120
Voidage of bed (%)	33.04	34.00	44.14
Strength (N/particle)	50	50	55
Average pore diameter (nm)	10.26	18.24	18.21
Pore volume ($cm^3 g^{-1}$)	0.46	0.68	0.63

2. Experimental

The hydrogenation of working solution in a trickle bed reactor containing very small particles of Pd/Al_2O_3 catalyst was investigated in this paper. The working solution was a mixture of eAQ, H_4eAQ, trioctyl phosphate and aromatics of C9–C10, there contained 22.1 g/L eAQ, and 116.5 g/L H_4eAQ, 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/m^3, 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 $\varphi 3 \times \varphi 2 \times 5$ (mm), the support was impregnated with $PdCl_2$ 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 (99.99%). 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