



Hydrogenation of 2-ethylanthraquinone with Pd supported on hollow ceramic microsphere catalyst: An experimental and kinetic study

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The catalytic hydrogenation of 2-ethylanthraquinone in the anthraquinone process of production of hydrogen peroxide gaining more interest to meet environmental demands of hydrogen peroxide as green oxidant. Noble metal palladium becomes a new category of catalyst due to their significant applicability in the catalytic hydrogenation reactions. Herein, wet impregnation method was used for synthesis of palladium supported on hollow ceramic microsphere catalysts. The palladium supported on hollow ceramic microsphere exhibits high catalytic selectivity, activity and stability in the liquid phase hydrogenation of 2-ethylanthraquinone. The reaction obeyed zero and first order kinetics with 2-ethylanthraquinone and hydrogen respectively. The average value of reaction rate constant observed was $2 \text{ mol L}^{-1} \text{ h}^{-1}$ and 6 L h^{-1} respectively. Highest yield of hydrogen peroxide obtained was 96.5% with a less consumption of 2-ethylanthraquinone.

Keywords: Hollow ceramic microsphere, palladium catalyst, 2-ethylanthraquinone hydrogenation.

Introduction

Hydrogen peroxide (H_2O_2) is one of the promising oxidant in various industries, particularly in the chemical and environmental protection industries¹. The world production of H_2O_2 by the auto-oxidation (AO) process of anthraquinone (AQ) in which 2-ethylanthraquinone (EAQ) working solution were obtained by dissolving EAQ in the organic solvents with the ratio of 1:1 (trioctylphosphate:trimethylbenzene) and hydrogenated into 2-ethylanthrahydroquinone (EAHQ). Then EAHQ is oxidized into H_2O_2 and EAQ back. Finally, H_2O_2 is extracted with water as an aqueous solution².

EAQ undergoing catalytic hydrogenation is the crucial step in AO route for production of H_2O_2 . US Patent, investigated the first commercial process for hydrogenation of EAQ in which, EAHQ was formed in a slurry reactor over a Raney nickel catalyst³. In recent years Al_2O_3 , SiO_2 , and $\text{SiO}_2\text{-Al}_2\text{O}_3$ are common oxide supports for palladium (Pd) catalyst used in the hydrogenation reactions^{4,5}. The development of the existing catalyst using suitable supports is necessary for pro-

cess improvement^{6,7}. Although extensive efforts have been made in the development of the hydrogenation step in the AQ process, there are still problems in reaction kinetic and order of the reaction. In the past literatures, the hydrogenation reaction was following zero and first order with respect to the EAQ and H_2 concentrations respectively⁸. Santacesaria *et al.*, investigated that the hydrogenation of EAQ over Pd catalyst was a very fast reaction and overall reaction rate was the rate controlling step for mass transfer resistance⁹⁻¹¹. Hence, design of catalyst is important and need of the hour to minimize the mass transfer resistance for hydrogenation reaction of EAQ.

In the present work, Hollow Ceramic Microsphere (HCM) based palladium catalyst was synthesized using wet impregnation method. High pressure autoclave reactor was used to study the catalytic activity of the synthesized catalyst.

Methods:

HCM having average diameter ranging from 5 to 500 μm was selected to support Pd. The Pd was supported on HCM

by a wet impregnation technique using PdCl₂ as Pd precursor.

Experimental

Hydrogenation of EAQ:

High pressure autoclave reactor was used for carrying out hydrogenation of EAQ with 50 mL (Amar Equipment, India) at 75°C, 0.3 MPa, 500–1500 rpm.

Determination of kinetic properties:



The EAQ hydrogenation reaction is represented by the following reaction kinetics as given by eq. (1)

$$-r = -\frac{dc}{dt} = k[C_{\text{EAQ}}]^0 \left[\frac{P_{\text{H}_2}}{RT} \right]^1 \quad (2)$$

The overall consumption rate and rate of hydrogenation of EAQ and H₂ consumed per unit time is calculated using eq. (2). 30 ml of EAQ solution with a catalyst concentration within a range of 0.2–0.8 g was used in each of the experimental batch. Hydrogenation time played vital role in controlling the rate of hydrogenation of EAQ over Pd catalyst was estimated through eq. (3).

$$-r_{\text{EAQ}} = -\frac{dC_{\text{EAQ}}}{dt} = k[C_{\text{EAQ}}]^0 \quad (3)$$

$$-r_{\text{H}_2} = -\frac{dC_{\text{H}_2}}{dt} = -\frac{dP_{\text{H}_2}}{(RT).dt} = \frac{k}{RT} [P_{\text{H}_2}]^1 \quad (4)$$

The conversion, yield, efficiency and selectivity of EAQ (x) is given by eqs. (5), (6), (7) and (8) respectively^{12–14}.

$$x_{\text{EAQ}} (\%) = \frac{n_0(\text{EAQ}) - n_1(\text{EAQ})}{n_0(\text{EAQ})} \times 100 \quad (5)$$

$$y_{\text{H}_2\text{O}_2} (\%) = n_{(\text{H}_2\text{O}_2)} / n_0(\text{EAQ}) \times 100 \quad (6)$$

$$B = \frac{5C_{\text{KMnO}_4} \times V_{\text{KMnO}_4} \times M_{\text{H}_2\text{O}_2}}{2V} \quad (7)$$

$$S = \frac{n_1(\text{EAQ}) + n_{(\text{H}_2\text{O}_2)}}{n_0(\text{EAQ})} \times 100 \quad (8)$$

Results and discussion

Characterization of catalyst:

Presence of metallic Pd in the Pd coated HCM was ascertained through X-ray diffraction (XRD) analysis. XRD patterns of supported HCM catalyst is presented in Fig. 1, representing that the Pd/HCM was chiefly consists of amorphous glass and aluminosilicate crystals. Pd peaks in the XRD patterns confirms the presence of Pd. It was in agreement with XRD of Pd corresponding to the, (111), (200) planes of Pd metal indicating the crystalline structure of prepared catalyst¹⁵. The calculated average particle size of Pd nanoparticles was 3.247 nm.

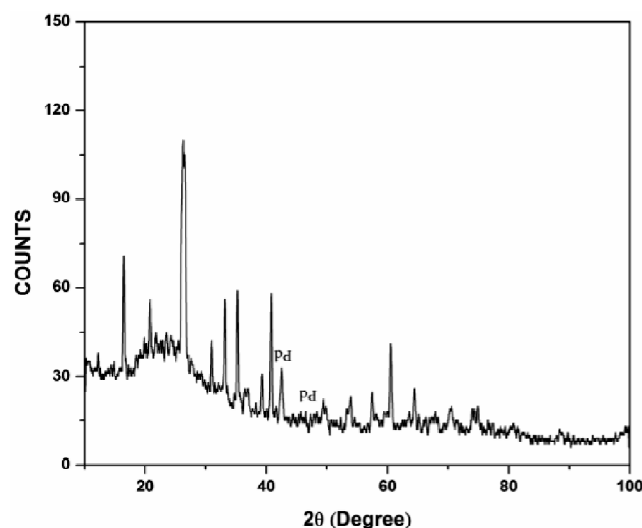


Fig. 1. X-Ray diffraction patterns of synthesized Pd/HCM catalyst.

Fourier Transform Infrared spectroscopy (FTIR) was performed for Pd supported catalyst and the catalyst after the hydrogenation reaction within the range 4000 to 400 cm⁻¹. Fig. 2a, shows the IR spectrum of Pd supported catalyst and the broad band present at 1085 cm⁻¹ shows the Si-O-Si vibrations¹⁶. IR-spectrum of catalyst after the hydrogenation reaction is shown in Fig. 2b. The 1622 cm⁻¹ band was due to asymmetric stretching of Si-O-Si. The hydroxyl groups on the catalyst surface presented in the IR spectrum of used catalyst, which shows a broad intense band at 3433 cm⁻¹, whereas the peak at 1622 cm⁻¹ was attributed to bending mode (δO-H).

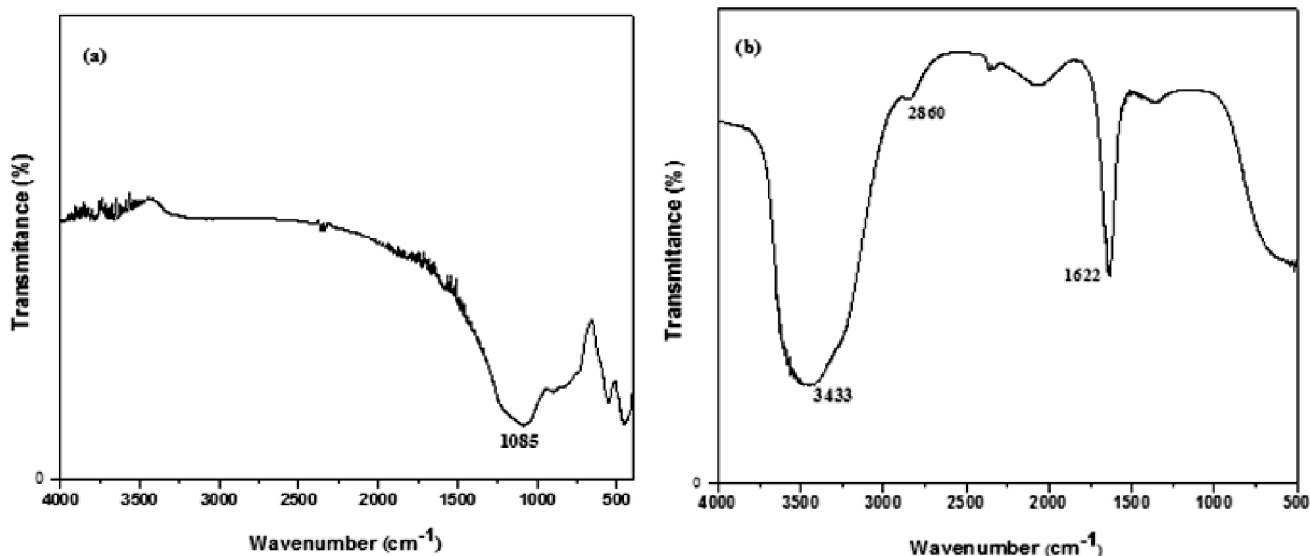


Fig. 2. FTIR spectrum of Pd/HCM catalyst before (a) and after (b) hydrogenation.

FESEM image of pretreated HCM is presented in Fig. 3, showing that HCM had spherical morphology and smooth surface. From Fig. 3 observed that some small pores are available on the surface of HCM and it was covered with Pd nanoparticles with a size ranging from 118–210 nm. An EDX band shows that the HCM were mostly consists of mixture of SiO₂ and Al₂O₃ (Fig. 4).

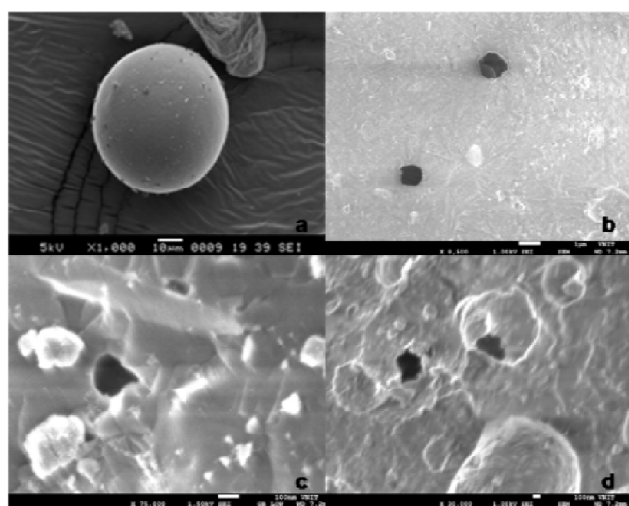


Fig. 3. FESEM micrographs of (a) pretreated HCM, (b), (c) and (d) Pd/HCM catalyst reduced in H₂ at 80°C (magnification 1000, 8,500, 30,000 and 75,000).

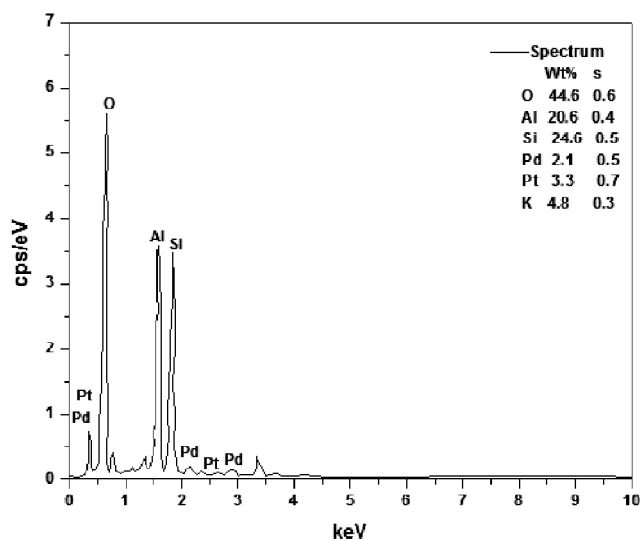


Fig. 4. EDX spectrum of Pd/HCM catalyst.

Catalytic performance test:

The catalytic hydrogenation test was performed with Pd/HCM catalyst (BET surface area 13.29 m²/g). The effect of total conversion on hydrogenation efficiency was studied (Fig. 5). The catalyst adsorbs hydrogen gas more easily if it supplies more electrons¹². Hence, the hydrogenation of EAQ over Pd/HCM catalyst improves catalyst activity and selectivity is maintained at 100%.

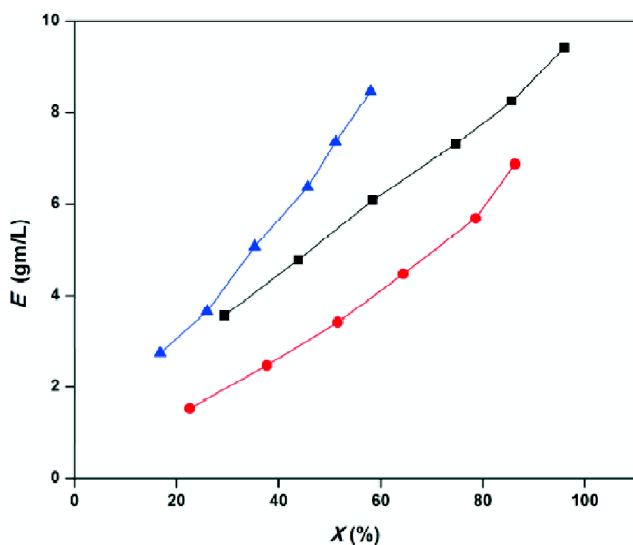


Fig. 5. Hydrogenation efficiency wrt total conversion of EAQ at different catalyst amounts (solution volume = 30 mL, @75°C, 0.3 MPa, within time span of 0.5–2.33 h, EAQ concentration (initial) of 109 g/L () 0.8 g, () 0.5 g, () 0.2 g).

Kinetic study:

Conversion of EAQ over 0.8 g catalyst was relatively higher than the lower catalyst dosages (0.2–0.5 g) which may be attributed to the saturation of active sites available for reaction corresponding to the available hydrogen partial pressure and solubility. The rapid diffusion of reactants in the porous structure of the catalyst and greater degree of dispersion leads to higher conversion of EAQ. Similarly, increase in the reaction time chiefly in the early stage of hydrogenation, increased the conversion of EAQ significantly. It demonstrates that the catalyst with HCM as support to Pd achieves its maximum conversion as high as 96% as compared to Al₂O₃ and SiO₂ support at the much reduced reaction time⁹.

The H₂O₂ yield was highest at 96% with 0.8 g catalyst when the hydrogenation time was 2.33 h. When the hydrogenation time was 0.5 h, the yield of H₂O₂ achieved was more than 50% with 0.2 g catalyst dosages. Table 1 depicted the experimental observations of the synthesized catalyst under different reaction conditions.

The hydrogenation of EAQ was observed to be zero order for EAQ concentration. Integral method was used to es-

Table 1. Pd/HCM catalyst performance in hydrogenation of EAQ

Catalyst dosage (g)	Conversion of EAQ (%)	Hydrogenation efficiency (g/L)	Selectivity (%)
0.8	96.0	9.4	100
0.5	86.3	8.3	100
0.2	58.3	6.8	100

timate the rate constant as per eq. (3)¹⁷:

$$-r = -\frac{dC_{\text{EAQ}}}{dt} = -\frac{k_2 C_{\text{EAQ}}}{1 + k_2 C_{\text{EAQ}}} \quad (10)$$

Plotting the data $-r$ vs C_{EAQ} yields a smooth curve. At higher concentration ($k_2 C_{\text{EAQ}} \gg 1$) the reaction follows zero order with a rate constant k_1/k_2 while at lower concentration ($k_2 C_{\text{EAQ}} \ll 1$), the reaction followed by first order kinetics with rate constant k_1 . Hence, eq. (10) can be written as:

$$\ln = -\frac{(C_{\text{EAQ}_0}/C_{\text{EAQ}})}{C_{\text{EAQ}_0} - C_{\text{EAQ}}} = -k_2 + \frac{k_2 t}{C_{\text{EAQ}_0} - C_{\text{EAQ}}} \quad (11)$$

k (rate constant) can be obtained by plotting

$$\left(\ln \frac{(C_{\text{EAQ}_0}/C_{\text{EAQ}})}{C_{\text{EAQ}_0} - C_{\text{EAQ}}} \right) \text{ against } \left(\frac{t}{C_{\text{EAQ}_0} - C_{\text{EAQ}}} \right) \text{ which gives a}$$

straight line having slope k_1 and y-intercept of line k_2 can be obtained as 2 and 6 respectively.

Catalytic mechanism:

In the catalytic mechanism of EAQ hydrogenation once synthesized catalyst was loaded at greater temperature field, nanosized pores were attached to each other converting into a bigger pores. It resulted in a high corrosion rate to erode the barriers between nanosized pores. The size of the nanopores was about 118–432 nm as can be seen in FESEM micrograph are shown in Fig. 3. The nanosize pores obtained on the surface of the Pd/HCM catalyst has significant effect on catalytic properties. The size of Pd particles is plays a vital role in controlling the activity of the catalyst and the smaller dimensions of Pd particles benefits the hydrogenation of EAQ¹⁸. The fundamental mechanism involved in the hydrogenation of EAQ has two steps: H₂ molecules activation and C=O activation in the EAQ structure. The outcomes of the previous studies show that the development of bigger

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pores on the surface of the catalyst was more active in the process of adsorption and activation of H₂ molecules^{19,20}. However, reports on performance of various Pd structure in the process of activation of EAQ is deficient.

Conclusions

Hydrogenation of aromatic compound EAQ over Pd/HCM catalyst was induced to a high conversion (96%) and the yield of H₂O₂ (96.5%) over less consumption of EAQ. XRD, SEM, BET and FTIR confirm crystalline structure of catalyst, higher Pd dispersion, specific surface area and the high electron density of the Pd/HCM catalyst. Catalytic activity (9.42 g/L) by maintaining the selectivity at 100% is maintained by the Pd/HCM synthesized catalyst. The hydrogenation of EAQ is found to be zero order for EAQ and first order for H₂ concentration respectively.

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Notations

- C_{EAQ} = concentration of EAQ (mol/L)
 C_{EAQ_0} = initial concentration of EAQ (mol/L)
 C_{H_2} = concentration of H₂
 C_{KMnO_4} = concentration of KMnO₄ solution (mol/L)
 k_1, k_2 = rate constants (mol/L·h) (L/h)
 $M_{\text{H}_2\text{O}_2}$ = molar mass of H₂O₂ (g/mol)
 $n_{(\text{H}_2\text{O}_2)}$ = moles formed (H₂O₂) (mol/L)
 $n_{0(\text{EAQ})}$ = initial moles of EAQ (mol/L)
 $n_{(\text{EAQ})}$ = moles of EAQ at time t (mol/L)

- P_{H_2} = partial pressure of H₂ (MPa)
 R = universal gas constant (8.314 J/(mol·K))
 $-r_{\text{EAQ}}$ = rate of consumption of EAQ (mol/h)
 $-r_{\text{H}_2}$ = rate of consumption of H₂ (h⁻¹)
 T = temperature (°C)
 t = time (h)
 V_{KMnO_4} = volume of KMnO₄ solution (mL)
 V = volume of H₂O₂ solution (mL)

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