Progress and prospective of heterogeneous catalysts for $\text{H}_2\text{O}_2$ production via anthraquinone process

Anjali A. Ingle¹ · Shahid Z. Ansari² · Diwakar Z. Shende¹ · Kailas L. Wasewar¹ · Aniruddha B. Pandit²

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Abstract
This paper reviews the improvement in the field of catalytic hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone for the successful production of hydrogen peroxide. Hydrogen peroxide is being used in almost all industrial areas, particularly in the chemical industry and in environmental protection, as the most promising oxidant for cleaner and environmentally safer processes. A variety of hydrogenation catalysts have been introduced for hydrogenation of 2-ethylanthraquinone in the production of hydrogen peroxide via anthraquinone (AQ) process. The aim of the present study is to describe the catalysts used in the hydrogenation of 2-ethylanthraquinone and the reaction mechanism involved with different catalytic systems. The hydrogenation of 2-ethylanthraquinone using metals, alloy, bimetallic composite, and supported metal catalyst with the structural modifications has been incorporated for the production of hydrogen peroxide. The comprehensive comparison reveals that the supported metal catalysts required lesser catalyst amount, produced lower AQ decay, and provided higher catalyst activity and selectivity. Furthermore, the replacement of conventional catalysts by metal and metal alloy–supported catalyst rises as a hydrogenation trend, enhancing by several times the catalytic performance.

Keywords Hydrogen peroxide · Anthraquinone process · Heterogeneous catalyst · Reaction mechanism

Introduction
Thenard, a French chemist, discovered hydrogen peroxide ($\text{H}_2\text{O}_2$) in 1818 (Chalmers 1996). The industrial manufacturing of $\text{H}_2\text{O}_2$ was introduced by reacting barium peroxide ($\text{BaO}_2$) with sulfuric acid, hydrochloric acid, and phosphoric acid in late 1885 (Van 1968). The demand for $\text{H}_2\text{O}_2$ is increasing constantly because of its favorable oxidation properties. It is an essential raw material for industrial green chemicals and environmentally friendly oxidizing agents (Jose et al. 2006; Yao et al., 2016a; Gema et al. 2016; Han et al., 2015a; Tan et al. 2012; Melada et al. 2006; Garcia-Serna et al., 2014). $\text{H}_2\text{O}_2$ is being used in various grades in the food storage and cosmetic and electronic industries. In the recent COVID-19 era, demand of healthcare products is increasing as $\text{H}_2\text{O}_2$ has high antiseptic properties which directly boost its market value. $\text{H}_2\text{O}_2$ is used as an antiseptic, which is commonly applied on the skin cuts and bruises to avoid infection. Furthermore, in light of the recent COVID-19 pandemic, demand for $\text{H}_2\text{O}_2$ has grown significantly worldwide due to its high consumption in the formulation of disinfectant products. $\text{H}_2\text{O}_2$ is the main ingredients in hand sanitizers whose demand has increased simultaneously all over the world.

The $\text{H}_2\text{O}_2$ has been used in the textile, food, mining, pulp, and paper industries and for the wastewater treatment. It is also used in the manufacture of printed circuit boards for semiconductors and also has good demand in aquaculture
market (Jose et al. 2006; Rosaria et al. 2016). The average plant capacity of H₂O₂ production was 20–40 kT per year with a world capacity of 1.5 million tons up to mid of 1990 (Ranganathan and Sieber, 2018). The plant capacity increases to 300 kT per year with a world capacity of 100% H₂O₂ which is around 5.5 million tons in 2015 (Ciriminna et al. 2016; Ranganathan and Sieber, 2018). The global producers of H₂O₂ involves Solvay (30%), Evonik (20%), and Arkema (13%) (Garcia-Serna et al. 2014).

**Production of hydrogen peroxide**

Autoxidation (AO) of anthraquinone (AQ), oxidation of primary and secondary alcohols, and electrochemical processes are the commercial processes for the production of H₂O₂ (Foller and Bombard, 1995). The direct introduction of hydrogen (H₂) and oxygen (O₂) over hydrogenation catalyst (Chen et al. 2013) semiconductor oxide photocatalytic reactions (Gabriele et al. 2003) and the incorporation of metal complexes in CO/O₂/H₂O mixture (Zudin et al. 1979) are the new synthesis processes for the production of H₂O₂. The different routes of the production of H₂O₂ are depicted in Fig. 1. However, the abovementioned processes carry the high risk of explosion and also suffer from low concentration of H₂O₂. Due to larger production scale and high concentration of H₂O₂, the AQ process overcomes the flaws of high energy consumption and larger production cost and surpasses all commercial processes with mild reaction temperatures and lower production costs. The conventional AQ process involved the sequential hydrogenation of an AQ derivative, mainly 2-ethylanthraquinone (EAQ), and the oxidation of 2-ethylanthrahydroquinone (EAQH₂). The world production of H₂O₂ is dominated by the AQ process in which EAQ is dissolved in a mixture of polar and non-polar solvents. The resulting working solution is hydrogenated to EAQH₂ in the presence of hydrogenation catalysts. EAQH₂ is then converted to H₂O₂ and EAQ after oxidation. A simplified production route of this AQ process is shown in Fig. 2. H₂O₂ is miscible with water in all proportions; hence, it can be recovered in extract phase by multiple washing of organic phase and enhances the concentration up to 50% by distillation process (Liu et al. 2005; Cheng et al. 2008). The overall world share of H₂O₂ production by the AQ process is about 98% (Guo et al. 2019).

The hydrogenation of EAQ in the presence of a catalyst is the key step in the production of H₂O₂ via the AQ process. I. G. Farbenindustries (1939) investigated the first commercial process in Germany for hydrogenation of EAQ in which EAQH₂ was formed in a slurry reactor over a Pd/Al₂O₃ catalyst (Goor et al. 1989; Kirchner 1979). The working solution was a combination of two organic solvents, namely benzene and a mixture of secondary alcohols (C7–C11). The concentration of the H₂O₂ solution obtained from the AQ process was about 0.6–1.8 wt%. It is important to enhance the efficiency of the AQ process by improving the purity of the
resulting H$_2$O$_2$ solution (Ren et al. 2011). Tang et al. (2014) describe the importance of catalyst support to enhance the diffusion rate as well as the dispersion of active metals. The spherical alumina has been used widely in the fixed bed reactor as catalyst support due to its excellent physical and chemical properties. Li et al. (2012) invented the Pd supported on whisker-modified spherical alumina, resulting in better catalytic activity than the convention pelleted catalyst.

This study is a review-based finding of different researchers, predominating on the hydrogenation of EAQ using Pd-supported catalysts. The focus is given on the progress in the research and development of the catalytic hydrogenation of EAQ for the production of H$_2$O$_2$ by the AQ process. The study discusses primarily the development in the field of new hydrogenation catalysts mainly oxide-supported catalysts for the AQ process. Furthermore, the preparation of Pd catalysts supported on Al$_2$O$_3$, SiO$_2$, and other novel catalyst systems was performed with an attempt to possibly elaborate the significant improvement in the literature. Thus, the present paper describes the advances in the preparation of Pd catalysts on various oxide supports and also other advanced catalysts with structured supports and summarized the general outlook of the developments in the associated area.

**Role of oxidizing agent**

An oxidizing agent (often referred to as an oxidizer or an oxidant) is a chemical species that tends to oxidize other substances, i.e., causing an increase in the oxidation state of the substance by making it lose electrons. Common examples of oxidizing agents include halogens (such as chlorine and fluorine), O$_2$, and H$_2$O$_2$.

Consumption of H$_2$O$_2$ is increasing day by day in the current forecast period and gaining importance as an environmentally friendly and efficient disinfecting agent because of the increased environmental awareness globally and more stringent legislative requirements. It can be added to the coloring liquid for efficient bleaching operation in the textile industry (Asghar et al. 2015; Karmakar 1999). It has been mixed with the reaction mixture to accelerate the oxidation reaction in an organosynthesis process for the production of fine and bulk chemicals (Sato et al. 1998). It is a promising substitute as an energy carrier used in the production of fuel cells because of its high density, safe handling, and easy storage (Yamazaki et al. 2008; Shaegh et al. 2012; Yamada et al. 2013; Yang et al. 2013). It can be united with a light source, catalyst, and ozone to remove various gaseous and aqueous pollutants from the effluent treatment plant. H$_2$O$_2$ is generally used in the wastewater treatment plant for wet peroxide oxidation, Fenton and photo-Fenton oxidations, sono-Fenton, electro-Fenton, and photocatalytic degradation reactions (Vieira et al. 2022; Perathoner and Centi, 2005; Rokhina and Virkutyte, 2010; Debellefontaine et al. 1996; Domingues et al. 2017; Gomes et al. 2010; Ribeiro et al. 2013, 2016, 2015). In situ generation of H$_2$O$_2$ or may be combining it with the photocatalytic water treatment process enhances the degradation of pollutants due to its promoting effect (Cui et al. 2012; Yao et al. 2016b; Kumar et al. 2017; Zhou et al. 2018; Deng et al. 2017).

In municipal wastewater treatment, H$_2$O$_2$ is used to remove hydrogen sulfide (H$_2$S) from the sewer pipes. It is mostly significantly used in an environmental application for the treatment of various types of industrial wastes. The H$_2$O$_2$ treatment can easily remove the cyanide, thiocyanate, nitrite, chloride, hypochlorite, and organic matter (Chidambara Raj and Quen, 2005). It can also be used in an advanced oxidation process involving more complex reactions as a source of hydroxyl radicals (Chidambara Raj and Quen, 2005; Vieira et al. 2020a, 2020b). H$_2$O$_2$ is used in the bulk sludge biological treatment as a source of oxygen and to prevent denitrification in the settling tanks. H$_2$O$_2$ can also be combined in the injection as a source of oxygen for microorganisms and nutrients to inject into the ground for in situ bioremediation of contaminated soils. H$_2$O$_2$ can be employed in the manufacturing of many organic and inorganic chemicals either directly or followed by conversion into a peroxycarboxylic acid using oxidation, epoxidation, hydroxylation, and oxohalogenation reactions, and for the initiation of emulsion polymerization reactions to produce chemicals like hydrazine, cyanogen, cyanogen chloride, bromine, iodic acid, high-purity ferric sulfate, perborates, percarbonates, benzyl peroxide, and lauryl peroxide (Centi et al. 2009; Bremner et al. 2000; Niwa et al. 2002; Jiajian et al. 2003; Ligtenbarg et al. 2003; Immanuel et al. 2003).

H$_2$O$_2$ can be used in a variety of applications in the mining and metal processing industry (Jennings et al. 2000). The major applications of H$_2$O$_2$ in the mining operations consist of extraction, separation, and purification of uranium, chromium, copper, cobalt, tungsten, molybdenum, gold recovery, and other precious metals. H$_2$O$_2$ can also be used in the metal finishing process for etching, stainless steel pickling, and non-ferrous metal finishing. High-purity H$_2$O$_2$ is used in the electronic industry for cleaning germanium and silicon semiconductor wafers and etching printed circuit boards. In chemical and pharmaceutical syntheses, hydrocarbons, nitrogen oxides, and sulfur dioxide in H$_2$S coming from the exhaust gases can be removed by H$_2$O$_2$ (Jose et al. 2006).

**Hydrogenation of 2-ethylanthraquinone**

The hydrogenation of EAQ has been studied extensively using various kinds of catalyst. However, the modified Pd-based catalysts are the significant catalytic system. Therefore, the improvements in the existing structure of the
catalysts are the important point of consideration for the process development (Li et al. 2005; Cheng et al. 2008; Li et al. 2012; Isaka et al. 2016; Freakley et al. 2016; Hong et al. 2015; Kosydar et al. 2011; Drelinkiewicz et al., 2005, 2006a, b). In the conventional AQ process, Rn-Ni catalysts have been used in the hydrogenation of EAQ. Rn-Ni catalysts have been replaced by Pd-supported catalysts in the industry due to its higher catalytic activity and selectivity of active quinone observed in the hydrogenation reactions (Liu et al. 2001; Hou et al. 2004). The supported catalysts provide better catalytic activity due to a more effective surface area available with smaller catalyst particles and the higher active metal component dispersion. They are thermally stable and can undergo high temperature and carry higher specific surface area (Hermans and Geus, 1979). The Pd metal on various supports has been used in the hydrogenation of EAQ in both batch and continuous processes.

The supported catalysts are gaining recognition in the field of catalysis due to their superior catalytic performance. Zhang and co-workers (2017) proposed the hydrogenation of EAQ in presence of the bimetallic Pd-Ru catalyst on γ-alumina. Yuan et al. (2017) investigated the effects of synergistic forces due to the addition of second metal such as Co, Ag, and Cu to the conventional catalyst Pd/Al2O3 in the hydrogenation of EAQ. The performance of the supported catalysts has been enhanced due to the size, crystal facet, and electronic structure of Pd particles. Li and Luo enhanced the supports by alternate modification using various methods of preparations to increase the dispersion of metal for higher catalyst activity and selectivity (Tang et al. 2014; Li et al. 2012; Feng et al. 2010; Liu et al. 2002).

In the previous studies, the catalytic hydrogenation of EAQ has been done using the monometallic (Ni, Pd, Ag, Cu) and the bimetallic (Pd-Co, Pd-Ag, Pd-Cu) catalysts. The Ni-B catalysts have been used in the hydrogenation of EAQ, and the results show the influence of the support structure on the catalytic activity and selectivity (Liu et al. 2001, 2002). Ni-Al and Ni-Cr-B-supported catalysts have also been used in the hydrogenation of EAQ. Han et al. (2015a) focused on the modification of supports with the facet-controlled Pd nanocrystals in the hydrogenation of EAQ. A specific method to enhance the catalytic performance of Pd nanocrystals is to place specific highly active facets instead of single-crystal nanoparticles (Jin et al. 2012; Drelinkiewicz and Hasik 2001) and Kosydar et al. (2010) studied extensively to lead the high-performance catalyst for hydrogenation reaction. It was found that the modification in the existing Al2O3 or SiO2 support to enhance the adsorption properties may retard the rate of reaction in the “deep hydrogenation” stage due to the addition of Na2SiO3, polyaniline, or alkali metals such as Li, Na, K, and Cs (Kosydar et al. 2010, 2011; Drelinkiewicz and Hasik 2001; Drelinkiewicz et al., 2004a, b, 2005, 2007; Drelinkiewicz and Waksundzka-Gora, 2006a, b). It was also investigated that the dispersion of Pd metal enhances with a decrease in the diffusion resistance due to the modification in the pore structure of the support. Han et al. (2015a) have focused on the modification of supports with preparing the high-performance catalysts by enhancing the catalytic chemistry of the Pd-based catalysts.

Pd/γ-Al2O3 catalyst was synthesized by Chen et al. (2015) by plant-mediated strategy for hydrogenation of EAQ with the adsorption-reduction method. Pd-Au/Al2O3 catalyst with special structural and electronic properties shows better catalytic performance in the hydrogenation reaction of EAQ (Han et al., 2015b). A combination of impregnation (IM) and deposition-precipitation (DP) methods was incorporated for the preparation of the bimetallic Pd-Au/Al2O3 catalyst with higher performance for the hydrogenation reaction of EAQ. The mass transfer–controlled hydrogenation of EAQ in the presence of the Pd catalyst was carried out by Santacesaria et al. (1994a, b), and they observed it as a very fast reaction. The hydrogenation of EAQ was confirmed to be zero- and first-order kinetic with respect to hydrogen and EAQ concentrations, respectively (Shang et al. 2012; Santacesaria et al. 1999, 1988; Berglin and Schoon, 1981). The glass beads with an eggshell structure have been used to support Pd nanoparticles and found to be a new catalyst in the hydrogenation of EAQ. Na2SiO3 and MgSiO3 contents in glass beads resulted in its alkalinity, and hence, the glass beads with porous eggshell structure are well suited to combine with the Pd nanoparticles (Shen et al. 2011; Sun et al. 2008a, 2008b).

**Catalytic performance and reaction mechanism**

The supported catalysts for EAQ hydrogenation can be classified into three categories: (1) Al2O3-supported catalysts, comprised of noble metal Pd and bimetallic Pd (Pd-Ru, Pd-Au, and Pd-Ag) catalysts supported on Al2O3; (2) SiO2-supported catalysts; and (3) catalysts with advanced structure such as Al2O3-SiO2, ZrO2-γ-Al2O3, glass beads, functionalized SBA-15, and honeycomb cordierite monolith catalysts.

**Al2O3-supported Pd catalysts**

An extensive study on the investigations of hydrogenation catalysts with experimental runs and theoretical discussions was attempted in the past (Han et al. 2015a; Tang et al. 2014; Li et al. 2012; Drelinkiewicz et al. 2005; Shi et al. 2016). Although the various metal-based catalysts were used in the production of H2O2 by different methods, the Pd-supported catalysts provide a better hydrogenation effect among all...
catalysts. The various Pd catalysts supported on Al$_2$O$_3$ are presented in Table 1. Ulmann (1994) mentioned the H$_2$O$_2$ is produced by mixing 30% EAQ, 70% 2-ethyl-tetraydroanthraquinone (THEAQ), and organic solvents followed by hydrogenation and oxidation as depicted in Fig. 3. The kinetic of hydrogenation of EAQ can be affected by internal diffusion mass transfer limitation because of a very fast reaction occurring over the Pd catalyst in a semi-batch reactor. Hence, they studied the kinetic for hydrogenation reaction measuring in terms of hydrogen consumption and rotating speed. It can be observed that the kinetics follow a zero-order kinetic for hydrogen and a first-order kinetic for THEAQ. Thus, the kinetics confirm that the THEAQ hydrogenation follows the Rideal-Eley mechanism. The hydrogenation reaction over the Pd catalyst has great affinity; hence, dissociative adsorption of hydrogen on the Pd catalyst is very high (Santacesaria et al. 1988).

The necessity to add a fresh catalyst in the industrial reactor to enhance productivity is a relevant consequence due to catalyst poisoning. Here, two types of catalyst poisoning were observed: reversible poisoning with water molecules adsorbed on Pd catalytic sites and irreversible poisoning.

Table 1 Hydrogenation of EAQ using various Pd-supported catalysts

| Catalyst         | Process conditions | Synthesis methods                  | References          |
|------------------|--------------------|------------------------------------|---------------------|
| Pd/Al$_2$O$_3$   | 0.1 MPa, 70 °C     | Impregnation                        | Santacesaria et al. (1999) |
| Pd/γ-Al$_2$O$_3$ | 0.3 MPa, 40 °C     | Adsorption-reduction                | Chen et al. (2015)   |
| Pd/Al$_2$O$_3$   | 0.3 MPa, 45 °C     | Polyol method                       | Li et al. (2016a)    |
| Pd Al$_2$O$_3$   | 0.3 MPa, 70 °C     | EISA, HT, impregnation              | Yuan et al. (2016)   |
| Pd-Ru/γ-Al$_2$O$_3$ | 0.3 MPa, 60 °C | Facile incipient wetness impregnation | Zhang et al. (2017)  |
| Pd/γ-Al$_2$O$_3$ | 0.2 MPa, 50 °C     | 1-step synthesis                    | Han et al. (2015a)   |
| Pd-Au/Al$_2$O$_3$| 0.3 MPa, 60 °C     | Deposition-impregnation              | Han et al. (2015b)   |
| Pd/δ-Al$_2$O$_3$ | 0.1 MPa, 50 °C     | Oil column                          | Li et al. (2012)     |
| Pd/AAO@Al       | 0.1 MPa, 50 °C     | 2-step low-potential anodizing/impregnation | Hong et al. (2015)  |
| Pd/SiO$_2$      | 0.1 MPa, 21 °C     | Dry impregnation                     | Drelinkiewicz (1992) |
| Pd/SiO$_2$      | 0.5 MPa, 50 °C     | Impregnation, precipitation          | Drelinkiewicz et al. (2004a) |
| Pd/Al$_2$O$_3$  | 0.3 MPa, 70 °C     | Incipient wetness co-impregnation    | Yuan et al. (2017)   |
| Pd/Al$_2$O$_3$  | 0.2 MPa, 60 °C     | Impregnation                        | Shang et al. (2012)  |
| Pd/glass beads  | 0.3 MPa, 50 °C     | Ion exchange                        | Shen et al. (2011)   |
| Pd/Al$_2$O$_3$  | 0.1 MPa, 55 °C     | Impregnation                        | Kosydar et al. (2011) |
| Pd/ZrO$_2$-γ-Al$_2$O$_3$ | 0.2 MPa, 45 °C | Impregnation                        | Feng et al. (2008)   |
| Ni-B/γ-Al$_2$O$_3$ | 0.3 MPa, 60 °C | Impregnation                        | Hou et al. (2004)    |
| Pd/Al$_2$O$_3$, Pd/SiO$_2$-γ-Al$_2$O$_3$ | 0.1 MPa, 50 °C | Impregnation                        | Feng et al. (2010)   |
| Pd/ZAL          | 0.3 MPa, 75 °C     | Co-precipitation, impregnation      | Ingle et al. (2020b, 2021) |
| Pd/HCM          | 0.3 MPa, 75 °C     | Co-precipitation, impregnation      | Ingle et al. (2020a)  |

Fig. 3 Reaction scheme for cyclic reduction and oxidation of EAQ and THEAQ
with aromatic rings partially hydrogenated and precipitated with EAQ molecules on the catalyst surface. The ring hydrogenation reactions are given in Fig. 4. 2-Ethyloctahydro-9,10-anthrhydroquinone (H₈EAQH₂) cannot be converted into H₂O₂. Hence, the other intermediate reactions have to occur to give anthrones and dianthrones (Ullmann 1994). A modified reaction is given in Fig. 5. Santacesaria et al. (1994b) mentioned that the EAQ inhibited the formation of H₈EAQH₂. The ring hydrogenation reaction of the aromatic rings of EAQ molecules in the presence of the Pd catalyst follows a dual-site mechanism at lower temperature and pressure as shown in Fig. 6 (Santacesaria et al. 1999, 1995).

Chen et al. (2015) prepared the Pd/γ-Al₂O₃ catalysts by the adsorption-reduction method and used in the hydrogenation of EAQ. CP extract which was used for the adsorption-reduction method can also be treated as a reductive and protective agent in the hydrogenation of EAQ. They performed the several experiments to find the effect of various parameters like reaction temperature, pressure, hydrogenation time, Pd loading, the volume of working solution, the flow rate of H₂, and the support modified by pretreatment on the yield of H₂O₂ and active EAQ contents. It was found that the highest yield of H₂O₂ could be achieved at optimized values of the working solution of 10 mL, the hydrogenation time of 1.5 h, and the flow rate of H₂ of 40 mL min⁻¹ operated at 40 °C. The sufficient work had been carried out on the pretreatment with different alkali modifiers (Na₂SiO₃) on the γ-Al₂O₃-supported catalysts which show better catalytic activity (Drelinkiewicz et al. 2004a, 2004b). It was found that the different pretreated catalyst supports (HCl, NaOH, Na₂CO₃, and Na₂SiO₃) provide the different values of H₂O₂ yield with the enhancement of about 5–10%. However, Na₂SiO₃-pretreated supports provide the highest value of yield of H₂O₂ (96.4%). The pretreated catalyst supports can also reduce the formation of the degradation products.

Fig. 4 Reaction scheme for ring hydrogenation

Fig. 5 A simplified reaction scheme for hydrogenation of EAQH₂

Fig. 6 Schematic representation of the dual-site mechanism
2-Amyl anthraquinone (AAQ) was hydrogenated in the presence of the Pd catalyst prepared by the polyol synthesis method. The effect of the size of the catalysts has also been studied in terms of the selectivity of the catalyst. The production of H₂O₂ by the AQ process needs to be focused on the selectivity of the catalyst. The consumption of active quinone in the hydrogenation/oxidation process increases with the generation of degradation products, leading to the decrease in catalyst activity. The bigger size particles easily activate the C=O bond, though AAQ has a unique configuration with reaction centers to activate the carbonyl group or aromatic ring. Also, the larger size of the Pd catalyst promotes the rate of deactivation which may be attributed to numerous side reactions (Li et al., 2016a, b).

Similarly, Yuan et al. (2016) have used one-pot evaporation-induced self-assembly (EISA), and hydrothermal (HT) methods for the synthesis of a Pd/Al₂O₃ catalyst by using the typical synthesis process of impregnation. The one-pot synthesis method provides the higher specific surface area, precise mesopores with the confined distribution of the pores, and the Pd particles effectively encapsulated over the inner part of the mesopores of Al₂O₃. Most probably, Pd and Pd black catalysts with and without supports have been used after the Rn-Ni catalyst by most of the manufacturers (Edvinsson Albers et al., 2001). The size and dispersion of the Pd particles are the essential variables to decide the activity of the supported catalysts. The dispersion of the Pd particles depends upon some of the favorable conditions such as the higher surface area of the support, uniform pore structure, and smaller pore size distribution. The elemental characteristics of the supports affect the dispersion of the Pd particles, which depends on the catalyst precursors (Tang et al. 2014), preparation methods (Li et al. 2012, 2014; Hong et al. 2015), and chemical compositions (Feng et al. 2010) of the catalysts.

Drelinkiewicz and Waksmundzka-Gora (2006a, b) performed the hydrogenation of EAQ with various catalyst supports such as Pd/C, Pd/SiO₂, and Pd/Al₂O₃. It was found that the catalyst with alumina support provides the higher catalytic activity. The selectivity towards active quinone and the formation of undesirable products get affected by the acidity of the support, whereas the acidity of the Al₂O₃-supported catalyst decreases the formation of undesirable products and enhances the selectivity of hydrogenation reaction (Yuan et al. 2016). The alumina-supported metal oxide composites have been prepared by HT or EISA synthesis processes for the numerous applications in the catalysis (Xu et al. 2012). Yuan et al. (2016) systematically studied the hydrogenation of EAQ using four types of catalysts. The higher catalyst activity was observed in the hydrogenation reaction in case of smaller Pd particles size (Feng et al. 2010). However, the surface morphologies and the electronic state of Pd particles affect the catalyst activity more than the size of particles. Thus, the increase in the catalytic activity may be attributed to the greater electron density of Pd particles at the interface.
EAQ. Both Pd(100) and Pd(111) facets were simultaneously more active toward the hydrogenation of C=O and the activation of the aromatic ring in EAQ. Hence, single-Pd nanocrystals were prepared by one-step synthesis and used in the hydrogenation of EAQ (Tan et al. 2012). It can handle the Pd(100) facet exposure and enhance the stability of Pd metal components. The principal mechanism of hydrogenation reaction of EAQ involved two important steps: the activation of the C=O bond of the aromatic ring of EAQ and adsorption of H$_2$ molecules. The previous studies reveal that the low-coordinate Pd(111) facet is less active in the adsorption and activation of H$_2$ molecules than the perfect Pd(100) facet. However, there are no studies related to the activation of EAQ by Pd catalysts. Figure 9 describes the modified adsorbed structures of EAQ over the Pd(100) and the Pd(111) facets. The stability of the Pd catalyst was found to be improved due to an increase in the interactions between the support and the nanocrystals formed by using the one-step synthesis method.

The incorporation of Au into the Pd/Al$_2$O$_3$ catalyst with the combination of IM and DP methods can enhance the catalytic activity and selectivity for the hydrogenation of

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Fig. 7 DFT-optimized structures of EAQ (down left), adsorbed EAQ on perfect (a) and defective (b) and e Pd(111) facets. Red, gray, white, and blue spheres represent O, C, H, and Pd atoms, respectively (light blue stands for the top layer) (Yang et al. 2012) (reprinted with permission)

Fig. 8 The proposed mechanism of promoting effect of a second metal in bimetallic Pd-Ru/γ-Al$_2$O$_3$ samples and the preferential modes of 2-ethylanthraquinone activation on their surface (Jin et al. 2012). Reprinted with permission
EAQ (Han et al. 2015a). Au remained inactive for the EAQ hydrogenation which was confirmed by the negligible yield of 1.11 g L\(^{-1}\) for the Au/Al\(_2\)O\(_3\) catalyst. It indicates that the Au atom was neutral, but after loading with the Pd atom, it could provide a significant amount of charge transfer to the Al\(_2\)O\(_3\) surface, leading to enhancement of the oxidation of Pd. When Au was being added to the Pd/Al\(_2\)O\(_3\) catalyst, the Pd/Au/Al\(_2\)O\(_3\) (14.27 g L\(^{-1}\)) and Au/Pd/Al\(_2\)O\(_3\) (12.79 g L\(^{-1}\)) catalysts have exhibited higher hydrogenation efficiency than Pd/Al\(_2\)O\(_3\) (12.04 g L\(^{-1}\)). Li et al. (2012) developed highly dissipated Pd/Al\(_2\)O\(_3\) catalysts with large surface area and the flower-like shape design whisker alumina supports. The alumina crystallites can be activated on top of the alumina surface after the evolution of OH\(^-\) ions by decomposition of urea. Then, activated Al\(^{3+}\) mixed with an aqueous solution of NH\(_3\) and CO\(_2\) to form ammonium aluminum carbonate hydroxide NH\(_4\)[Al(OOH)HCO\(_3\)] nanocrystals. The higher hydrogenation efficiency and selectivity of EAQ hydrogenation is reported with whisker-modified alumina supports. The diffusion is the main driving force for the reaction to occur. The external and internal mass transfers for the hydrogenation reaction of EAQ by using various heterogeneous catalysts, mainly supported Pd catalysts, usually depend upon the shape and pore structure of the support. The performance of the Pd/AAO@Al catalysts in the hydrogenation of EAQ has been enhanced due to the confined effect of cylindrical-shaped pores arranged in a highly ordered array in the AAO support with narrower diffusion distance.

The hydrogenation of AQ and THAQ can be estimated using DFT calculations. The cluster models (Christmann, 1988; Baykara et al. 1986; Rochefort et al. 1990; Roques et al. 2001, 2007; Bertin et al. 2005) and slab models (Dong et al. 1996; Kamachi et al. 2013) were used to investigate the behavior of the Pd(111) facet (Kamachi et al. 2015). The Pd atoms can adsorb atomic H\(_2\) to form H\(_2\) atoms with the two neighboring 3-fold hollow fcc positions. The H\(_2\) dissociation is facile, and the adsorbed AQ remains at the bridge sites on the Pd(111) surface (Kamachi et al. 2015). Thus, anthrahydroquinone (AHQ) and tetrahydroanthrahydroquinone (THAHQ) could be formed with the combination of the two carbonyl O\(_2\) atoms of AQ and THAQ with the surface H\(_2\) atoms. The Pd catalyst with various supports (C, SiO\(_2\), and Al\(_2\)O\(_3\)) has been used in the hydrogenation of AQ and THAQ to form AHQ and THAHQ (Santacesaria et al. 1994a, 1994b; Albers et al. 2001; Fajt et al., 2008). The hydrogenation of THAQ is reported as more productive than that of AQ to convert into THAHQ and the degradation of
AQ and THAQ to form degradation products such as tetrahydro-anthrone (THAN), anthrone (AN), tetrahydro-oxanthrone (THOAN), and oxanthrone (OAN) which were slow (Santa-cesaria et al. 1988). Hence, demand is growing for process intensification for an industrial AQ process where the side reactions could be suppressed.

**SiO₂-supported catalysts**

Silica supports have been used in the field of catalysis due to its excellent properties. Highly dispersed catalysts can be prepared using silica as supporting material. It has enormous properties like high surface area and high pore volume, and the mesoporous channels make them comfortably used for impregnation of metal catalyst for better adsorption and dispersion of metal salt and trap active metal particles that can resist deactivation during the reaction.

Hydrogenation of EAQ by using the Pd/SiO₂ catalyst has been carried out with almost 100% selectivity in a slurry reactor. Drelinkiewicz (1992) investigated the effect of catalyst dosages on the rate of hydrogenation, the yield of EAQH₂, and the formation of the degradation products. It indicates that the formation of EAQH₂ is dependent on the intermediate product H₂EAQH₂. It was found that the average value of degree of hydrogenation for the generation of degradation products can be evaluated from the individual degree of hydrogenation (U). The value of U changes during reaction, depending on the amount of catalyst. Hence, the formation of degradation products or undesirable products due to side reaction depends on the catalyst concentration.

The selectivity towards active quinone in the hydrogenation of EAQ can be determined by the concentration of H₂ on the surface of the catalyst and the type of reaction regime used. Mainly, two types of reaction regimes can be used in the hydrogenation reaction such as kinetically controlled and diffusion-controlled regimes. The “hydrogen poor” mode has observed when the rate of reaction was associated with the rate of H₂ transport. However, the “hydrogen-rich” mode existed when the rate of the chemical reaction was interpreted by the overall reaction rate. Ni catalyst has been dealt with the hydrogenation of AQ under high pressure of H₂ with the quantitative formation of AN. Hydrogenation of AQ on Pd/Al₂O₃ and Pd/SiO₂-Al₂O₃ could also form H₂EAQ and other unidentified products. Drelinkiewicz (1992, 1995) investigated in the deep hydrogenation of AQ that the temperature, the catalyst dose, and the grain size can manage the internal diffusion, or external mass transport processes and the chemical reaction. The different reaction regimes can have different impacts on the hydrogenation reaction and, more specifically, the yield of H₂EAQ. The yield of H₂EAQ increases when the external mass transport is the driving force for the reaction kinetics involved (Binder et al. 2009).

Drelinkiewicz et al. (2004a, b, 2005, 2007) studied extensively the SiO₂ and Al₂O₃-supported eggshell catalysts with various types of supports and Pd concentration profile in the hydrogenation of EAQ. The precipitation technique was used to precipitate palladium hydroxide onto SiO₂ and Al₂O₃ supports to prepared catalysts which were then impregnated with various alkaline (NaHCO₃, NaH₂PO₄, Na₂SiO₃) solutions. The SiO₂-supported catalyst provides poor deactivation than the Al₂O₃-supported catalysts, whereas the SiO₂-Al₂O₃-mixed supported catalyst with Na₂SiO₃ impregnation gives the better catalyst activity (Drelinkiewicz et al. 2004a, 2004b, 2006a,b).

The hydrogenation of EAQ has also been found to be affected consequently by the humidity. The humidity plays a crucial role in the hydrogenation reaction, the dissociation of EAQ to EAQH₂, and also the conversion of EAQH₂. The utilization of EAQH₂ and desirable and undesirable products varies depending upon the alkalinity of Pd/SiO₂ catalysts. The humidity dominates the process of EAQH₂ transformation with less-alkalinity Pd catalysts.

**Advanced catalytic systems**

The mass transfer of EAQ in the hydrogenation of EAQ using the Pd catalyst is a fast reaction and rate-controlling step (Santa-cesaria et al. 1988). On this prediction, Feng and co-investigator (2010) performed the hydrogenation of EAQ in a slurry reactor using the newly synthesized catalyst Pd/SiO₂-Al₂O₃, which can attain 10.3 g L⁻¹ of the yield of H₂O₂. Shen et al. (2011) achieved 11.2 g L⁻¹ of the yield of H₂O₂ with a Pd/eggshell glass catalyst. The particle size can be controlled by varying the reflux timing and the calcination temperature (Yuan et al. 2016). As catalytic properties of catalyst depend upon the surface structure and particle size, the focus on the design of catalysts is desirable for well-defined highly dispersed particles. The correlation between the particle size and the reaction activity or selectivity has been introduced by various authors (Binder et al. 2009; Zhou et al. 2006).

Eggshell structure catalysts used in the hydrogenation of EAQ decrease the diffusion distance to enhance the reaction rate. Carbon or Al₂O₃ supports have been used for the commercial Pd catalysts in the conventional processes. The acidity of the support material has imparted a specific role in the hydrogenation reaction. Shen et al. (2011) have used eggshell-structured glass beads to support the Pd catalyst. They have used subcritical water treatment as the pretreatment of support and the ion exchange method for loading Pd metal. The hydrogenation reaction was performed in a fixed-bed reactor packed with a Pd-supported eggshell catalyst. The metal ions contained in glass beads exchange with the metal ions with higher electronegativity. Sixty percent of conversion of EAQ was achieved in less than 2 s at a liquid.
flow rate of 0.6 mL min⁻¹, gas-to-liquid ratio of 30, and Pd loading of 0.34 wt%. The space-time yield (STY) and hydrogenation efficiency were found to be 3800 g H₂O₂ L⁻¹ h⁻¹ and 11.2 g H₂O L⁻¹, respectively. A similar study has been done by Yao et al. (2016a) for the hydrogenation of EAQ by using the eggshell structure of the Pd catalyst in a fixed-bed reactor. In situ prepared catalyst has a diameter of 100 μm, shell thickness of 3–4 μm, and small mono-dispersed Pd nanoparticles ranging from 4 to 5 nm. The hydrogenation efficiency of 6.6 g L⁻¹ and the yield of H₂O₂ of 35.5% were obtained at an optimum Pd content of 0.32% and a residence time of less than 4 s. Thiele modulus and effective internal diffusion factors were used to know the effect of internal diffusion resistance. It was found that it weakens the internal diffusion resistance at fast reactions. The STY for hydrogenation reaction was found to be 567.5 g H₂O₂ L⁻¹ h⁻¹ at the liquid flow rate of 0.2 mL min⁻¹ and the gas-to-liquid ratio of 30.

The monolithic catalysts have been used extensively in various catalytic reactions. The basic characteristic of the ideal monolithic catalyst consists of enough durability, high specific surface area, and catalytically active phases. The structure of the porous layer plays an important part in the enlargement of the surface area of the catalyst and affects the active phase required for catalysis. The catalytically active phase in the monolithic catalyst improves the active sites needed for chemical reactions due to its high distribution capacity. Zhang et al. (2008) compared a novel Pd/Al₂O₃/cordierite monolithic catalyst with the Pd catalyst having Al₂O₃ coating. It was found that the STY of H₂O₂ over a monolithic catalyst is better than that of commercial catalysts with only Al₂O₃ coating. In the hydrogenation of EAQ using the monolithic catalyst, the diffusion distance is very short which improves the diffusion of the active metal. Li et al. (2015) have performed the 1000-h-long stability runs and determined that the monolithic catalyst with SiO₂ coating (PSC) provides better catalytic activity than the Al₂O₃ coating (PAC). The regular structure and weak acidity of the PSC monolithic catalyst made them durable in such a long test. The yield of H₂O₂ increases up to 5.5 g L⁻¹ with the incorporation of MgO to the SiO₂ wash coat (Li et al. 2016a, b). It was also investigated that the mass transfer distance was very short and the mass transfer resistance also becomes less in the case of monolithic catalyst, leading to the improved hydrogenation efficiency. Thus, the application of a monolithic catalyst in the hydrogenation of EAQ has an important contribution.

Shi et al. (2016) investigated the Pd/oxide/cordierite monolithic catalysts prepared by the impregnation method. The Al₂O₃ layer with about 6 μm of the modest thickness in the prepared catalyst was used in the flowing tube reactor catalyst for hydrogenation of EAQ. The highest conversion of EAQ was found to be 99.1%, and the hydrogenation efficiency was found to be 10.0 g L⁻¹. It resulted to the successful Pd penetration and the wider pore size, which promotes the distribution of Pd and receptiveness of the active sites by the reactants. The catalyst activity generally depends upon the type and thickness of the oxide layer. The catalyst with γ-Al₂O₃ as a layer gives higher reactivity than SiO₂ and SiO₂-Al₂O₃ as layers.

The metal-organic frameworks (MOFs) and modified zeolites have been introduced for the hydrogenation of EAQ. The ordered structure, higher surface area, and constant distribution of pore size of the zeolites (e.g., MCM-41 and SBA-15) make them better to support Pd nanoparticles and reduce the diffusion resistance. It enhances the surface for systematic dispersion of metal in the three-phase catalytic reactor (Beck et al. 1992; Kresge et al. 1992; Tanev and Pinnavia, 1996). Guo et al. (2017) determined the pore diameter of zeolites (MCM-22 and Beta) and the effect on the EAQ hydrogenation. It was found that the monolithic catalyst (0.8% Pd/MCM-41/COR) demonstrated the highest yield of H₂O₂ (7.54 g L⁻¹) and selectivity (85.3%) in the production of H₂O₂ by AQ process. The efficiency of 0.8% Pd/MCM-41/COR monolithic catalyst (157.3 g H₂O₂ gPd⁻¹ h⁻¹) was much higher than that of a commercial pellet catalyst (500 g H₂O₂ gPd⁻¹ h⁻¹). The monolithic catalysts possess higher mass transfer coefficients (5–20 times) than the commercial catalyst. Guo et al. (2016) have presented the hydrogenation of EAQ using monolith catalysts (Pd/SiO₂/COR) with low-pressure drop which has a great impact on the mass transfer performance than the commercial pellet catalyst. It was found that the maximum STY obtained was 793.2 g H₂O₂ gPd⁻¹ h⁻¹ with 1.5% Pd/SiO₂/COR catalyst at 80 °C and atmospheric pressure.

Cai et al. (2019) prepared the nanorod by adding EAQ to aluminum isopropoxide (AIP) and isopropyl alcohol (IPA). The characteristics of the support, structure of the catalyst, metal distribution, and the interactivity of the metal and the support are necessary factors to enhance the catalytic activity of hydrogenation reaction (Augustyn et al. 2010). The modification of the support is generally used to enhance catalytic activity. The results reveal that the addition of a certain fixed amount of EAQ (4 wt%) in the hydrogenation step helps in the modification of the textural properties of the supports. The hydrogenation efficiency is reported to improve from 7.49 to 10.28 g L⁻¹, which is 37.3% higher than the catalyst prepared without incorporation of EAQ. The formation mechanism of the Pd/γ-Al₂O₃ catalyst is shown in Fig. 10. In this, EAQ was added to AIP and IPA and followed by the vigorous blending. Hydrolysis of AIP converts it into γ-AlOOH during the sol-gel process. In the aging process, the EAQ molecules were adsorbed on the crystals formed. The recognition effects of the addition of the structure-directing agent (EAQ) before the formation of
Al(OH)$_3$ and separation after calcination (550 °C) towards γ-AlOOH (Li et al. 2013) generate a definite pore structure over the commercially used γ-Al$_2$O$_3$ supports.

Nano-hybrid catalysts (bimetallic and trimetallic) have been used for various hydrogenation reactions (Chen et al. 2015; Hong et al. 2017; Carvalho et al. 2004; Suresetty et al. 2010; Hungria et al., 2006; Toshima et al. 2007; Adams et al. 2007; Liew et al. 2019). The novel nano-hybrid trimetallic catalyst support Zr-Al-La (ZAL) was synthesized by co-precipitation and impregnated with Pd by an incipient wetness impregnation method (Ingle et al., 2020a, b, 2022). The hydrogenation reaction was performed in a high-pressure autoclave reactor with Pd supported on ZAL catalyst. The co-precipitation by the direct contact of oxide supports gained much attention due to its accessibility and economy. By this method of the preparation of trimetallic oxide support which precipitates with small size, narrow size distribution and high crystalline structure may be obtained. Pd/ZAL catalyst improves the catalytic activity (9.15 g L$^{-1}$) and provides the high selectivity (100%) simultaneously, which has ascendancy over existing processes. The hydrogenation of 2-EAQ provides the conversion as high as 93% with only 0.5 g of the catalyst with a hydrogenation efficiency of 9.15 g L$^{-1}$ at operating conditions of 75 °C and 0.3 MPa.

The size of Pd particles plays a vital role in controlling the activity of the catalyst, and the smaller dimensions of Pd particles benefit the hydrogenation of EAQ (Feng et al. 2010). The Pd supported on hollow ceramic microsphere (HCM) exhibits high catalytic activity, selectivity, and stability in the liquid-phase hydrogenation of EAQ (Ingle et al. 2020, 2021). Catalytic activity was found to be 9.42 g L$^{-1}$ with 100% selectivity over the Pd/HCM catalyst. The calculated mass transfer resistance of the reaction over the Pd/Zr-Al-La catalyst was found to be moderate with a diffusion coefficient of the reactant (H$_2$) of 0.0133 × 10$^{-6}$ m$^2$ s$^{-1}$ at 75 °C. It was also verified and confirmed with the Thiele modulus (calculated as 0.0289) indicating no mass transfer resistance. The effectiveness factor ($\eta_s$) was found to be 1.0, indicating the negligible mass transfer resistance in the hydrogenation reaction using the Pd/HCM catalyst.

Ma et al. (2019) grafted silica support (SBA-15) with alkyltriethoxysilane to support commercial Pd catalysts. The silica supports can be functionalized by grafting method with alkyltriethoxysilane and deposition of Pd by the incipient wetness impregnation method. Both the grafting sequence and the grafting amount were varied over each hydrogenation cycle. It was reportedly found that the grafting agent improves the catalytic activity by increasing the hydrophobicity of the silica support. The effect of grafting amount in the hydrogenation of EAQ over Pd/SBA-15 catalysts provides better performance. The highest grafting amount of catalysts gives the enhancement in the activity and the selectivity of the hydrogenation reaction (98.3%).

**Conclusions**

The hydrogenation of EAQ into EAQH$_2$ for the production of H$_2$O$_2$ gains more interest to meet the environmental demands of H$_2$O$_2$ as a green oxidant. The commercial production of H$_2$O$_2$ by the AO process proposed in Germany in the late 1930s has been used for large-scale production. The homogeneous catalysts (Ni, Cu, and Pd) have been used by many researchers in the hydrogenation of EAQ for the commercial production of H$_2$O$_2$ from the AO process, and it provided the satisfactory activity and selectivity. Moreover, the separation and regeneration of the catalysts were still complicated. Intensification and investigation of reaction mechanisms of the AO process are the utmost important issues for the technical development of liquid-phase
hydrogenation of EAQ in the presence of the Pd catalysts. Thus, the development of heterogeneous catalyst is relatively secondarily recognized in the field of catalysis. The development of the heterogeneous catalysts in the hydrogenation reactions is looked forward to increase the production of $\text{H}_2\text{O}_2$, as the heterogeneous catalysts were not used for commercial production of $\text{H}_2\text{O}_2$. Nonetheless, the $\text{H}_2\text{O}_2$ process needs to fortify further in wholesomeness. Therefore, the heterogeneous catalysts are designed to have better stability, easy separation, safe handling, regeneration of the catalyst, and the reactor designing, which optimized the costs of commercial production of $\text{H}_2\text{O}_2$.

The alumina-supported catalysts can be significantly applied for the production of $\text{H}_2\text{O}_2$ by the AQ process and in the direct synthesis of $\text{H}_2\text{O}_2$. The Al$_2$O$_3$-supported catalyst provides an enhancement in the efficiency of $\text{H}_2\text{O}_2$ synthesis in the AQ process. Al$_2$O$_3$-supported catalysts are reported to provide more yield of $\text{H}_2\text{O}_2$ than the conventional Ni- and Pd-based catalysts. These catalysts can show high activity than the conventional Pd catalysts. Bimetallic catalysts (Pd-Co, Pd-Ag, Pd-Cu, Pd-Au, Pd-Ru, Pd-La), amorphous alloys, and facet-controlled Pd nanocrystal catalysts gave better hydrogenation efficiency than the commercial pellet catalysts. The novel metal catalysts generally provide much higher activity in contrast with the oxide-supported catalyst at lower reaction temperatures. Furthermore, Pd-based catalysts with stronger interactions between promoter and the major component, definite structure, better metal dispersion, and superfine particle exhibits higher selectivity, stability, and catalyst activity in the hydrogenation of EAQ. Disregarding with process development in the structure of the catalyst, one must be focused on developing reactors designed to intensify the activity and selectivity of EAQ hydrogenation. In recent years, the fluidized-bed reactor has become the substitute for a fixed-bed reactor. The fluidized-bed reactor has been a trending technology with important findings used in the hydrogenation reaction of EAQ for the production of $\text{H}_2\text{O}_2$. Sinopec has developed hydrogenation reaction by using bimetallic supported catalysts in the fluidized-bed and slurry stirring tank reactor for the production of $\text{H}_2\text{O}_2$ (Li et al. 2018).

Cordierite monolith catalysts exhibit much higher selectivity towards active quinones (> 99%) and can be obtained over Pd/$γ$-Al$_2$O$_3$/cordierite monolithic catalysts at the reaction temperature of 60 °C and atmospheric pressure, however at a lower yield of $\text{H}_2\text{O}_2$ (10 g L$^{-1}$). Furthermore, the nanocrystals of Pd metal with oxide support provide better catalytic activity. Thus, the high solidity of the abovementioned catalyst in the hydrogenation of EAQ forged them better than metal-based catalysts. The maximum $\text{H}_2\text{O}_2$ yield was reported up to 15 g L$^{-1}$ and was achieved over the Pd/Au/Al$_2$O$_3$ catalyst with 99.56% selectivity towards active quinones. Commercially, $\text{H}_2\text{O}_2$ can be produced from sequential auto-oxidation of EAQ with Pd-based catalysts, the technique which is often employed for useful production of $\text{H}_2\text{O}_2$. Nonetheless, numerous significantly active metal catalysts were employed for EAQ hydrogenation. The eminently promising hydrogenation catalyst with almost 100% selectivity was Pd/SiO$_2$. However, a substantial amount of investigation in the field of hydrogenation catalysts for EAQ hydrogenation has been carried out with analysis and theoretical interpretation, and the mechanism behind hydrogenation reaction is still invariance. The advancement in recent findings should have assuredly accentuated basic acknowledgment regarding the characteristics of active sites and the active component mutual actions of a catalyst booster including support mechanisms of reaction, which play a significant part in the highly effective catalyst designed for the hydrogenation of EAQ.

Availability of data and materials All the data and other materials are included in the published article.

Author contribution Anjali A. Ingle: contribution in the conceptualization, collection of the literature, data analysis, and writing of the manuscript. Shahid Z. Ansari: formation of the figures and tables and editing of the manuscript. Diwakar Z. Shende: review of and correction in the manuscript. Kailas L. Wasewar: critical review of and correction in the manuscript. All authors read and approved the final manuscript.

Declarations

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