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Synthesis of hydrogen peroxide over Pd/SiO₂/COR monolith catalysts by anthraquinone method

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ABSTRACT

In this work, a series of Pd/SiO₂/COR (cordierite) catalysts with different Pd contents were successfully prepared by impregnation method. The obtained Pd/SiO₂/COR catalyst samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), BET, hydrogen temperature programmed reduction (H₂-TPR), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) show that Pd element is mainly in the state of PdO, and 1.5% Pd/SiO₂/COR catalyst with the theoretical Pd content of 1.5% has the most PdO content on the monolith channel surface when compared to other Pd content monolith catalysts in this paper. Then in the experiment it was found the optimum catalyst is 1.5% Pd/SiO₂/COR, which is consistent with XPS results. The STY can achieve 793.2 g H₂O₂ g⁻¹ Pd h⁻¹ over 1.5% Pd/SiO₂/COR catalyst.

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1. Introduction

Hydrogen peroxide (H₂O₂) is an important green chemical raw material and product widely used as oxidant, bleach, disinfectant, deoxidizer, polymer initiator and crosslinking agent. Its applications include military, textile, papermaking, chemical, pharmaceutical, environmental protection, food industries, and others [1,2].

Previously, hydrogen peroxide was mainly prepared by hydrolysis of the ammonium peroxydisulfate. Today, more than 99% of hydrogen peroxide is commercially manufactured by the anthraquinone method, including the 2-ethyl-9,10-anthraquinone (eAQ) hydrogenation process and the autoxidation process of 2-ethyl-9,10-anthrahydroquinone (eAQH₂, one of products of eAQ hydrogenation process), while the catalytic hydrogenation of eAQ process is the key step [3–8]. As the target product of hydrogenation of eAQ process, eAQH₂ is formed in the quinone-hydroquinone stage but undergoes further hydrogenation reaction. The by-products mainly include 2-ethyl-5,6,7,8-tetrahydroanthracene-9,10-diol and 2-ethyl-1,2,3,4-tetrahydroanthracene-9,10-diol (H₄eAQH₂), and 2-ethyl-1,2,3,4,5,6,7,8-tetrahydroanthracene-9,10-diol (H₈eAQH₂). H₄eAQH₂ is the only desired compound among all of the by-

products, because it produces H₂O₂ in the autoxidation process. Meanwhile, H₈eAQH₂ does not produce H₂O₂, so it can be called non-active product [6,7,9,10–14].

The hydrogenation process requires a catalyst, and currently palladium-based pellet catalysts are mainly used in industrial applications [7,15–25]. Halder and Lawal [22] conducted the reaction in a microreactor with inner diameter 0.775 mm and the loading 13 mg supported Pd catalyst (1% Pd). Drelinkiewicz et al. [26] prepared hydrogen peroxide over palladium-based pellet catalyst in a turbulence reactor with the diameter 5.4 cm and the loading 19 g (25 cm³) supported Pd catalyst (2% Pd). Edvinsson et al. [27] reported the synthesis of H₂O₂ in a commercial slurry reactor at 55 °C and 200 kPa. In recent years, as a kind of novel catalysts, monolithic honeycomb catalysts are widely used in gas, liquid and multiphase systems due to their unique characteristics such as low pressure drop, high specific external surface area and effectiveness factor, minimum axial dispersion, and less catalyst attrition [28–32].

Structured catalysts may have great potential to improve the conversion or selectivity during the anthraquinone hydrogenation process [33,34]. Moreover, monolith catalyst has lower pressure drop and better mass transfer performance than the traditional pellet catalyst. In this work the palladium-based monolith catalyst using SiO₂ as the secondary carrier (i.e., Pd/SiO₂/COR monolith catalyst) was proposed for the catalytic hydrogenation of eAQ for the synthesis of H₂O₂, aiming to combine the advantages of palladium active centers (high activity) and monolith honeycomb support (low pressure drop and high capacity). Then, the prepared

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Pd/SiO₂/COR monolith catalysts were characterized by XRD, SEM, BET, H₂-TPR, ICP-AES, and XPS. Finally, the influence of different operating parameters (catalyst content, reaction temperature, pressure, flow rates of inlet H₂ and eAQ solution, and concentration of eAQ solution) on reaction performance was investigated to get the optimum condition for the synthesis of H₂O₂ over Pd/SiO₂/COR catalyst.

2. Experimental

2.1. Preparation of Pd/SiO₂/COR

A series of Pd/SiO₂/COR monolith catalysts were prepared using coating method according to the following four steps. 1) The pretreatment of cordierite monolithic support: the cordierite monolith samples with a diameter of 20 mm and a height of 10 mm were cut from a commercial honeycomb cordierite (φ 101.6 × 127 mm, 400 cpi square channels), and then pretreated using 15 wt% nitric acid solution at 80 °C for 4 h. Afterwards, the pretreated cordierite monolith samples were washed using deionized water to neutral, dried at 100 °C for 4 h and calcined in a Muffle furnace at 550 °C for 4 h; 2) The coating of SiO₂: the cordierite samples after acid treatment were immersed into the silicon sol solution for 5 min and then dried at 100 °C. The coating procedure was repeated several times. Then the samples (SiO₂/COR) were dried at 100 °C for 4 h and calcined at 550 °C for 4 h; 3) The coating of active catalyst Pd: the samples obtained in step 2) were immersed into the 6 mg·mL⁻¹ PdCl₂ aqueous solution, and then dried as the coating of SiO₂. The procedure was repeated several times to achieve the desired coating amount of Pd. Thus, a series of PdCl₂/SiO₂/COR precursors can be obtained; 4) The activation of precursor: the precursor was calcined at 550 °C to remove the chlorine element, and the Pd/SiO₂/COR monolith catalysts were obtained. The theoretical content means that the Pd in the solution is all supported onto the catalyst based on theoretical calculation for loading target content.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected from a Bruker D8 Advance X-ray diffractometer (40 kV, 40 mA) using Cu-K α radiation (λ = 0.15418 nm). Data were recorded in the 2θ range from 5° to 50° with a step size of 5° and a count time of 1 min per step.

Scanning electron microscopy (SEM) micrographs were recorded on a JEOL JSM-6701F microscope working at 5.0 kV accelerating voltage. Before observation, the samples were subsequently sputter coated with a thin gold film by an ion-sputtering instrument to make the sample conductive.

The Brunauer-Emmett-Teller (BET) specific surface areas of the catalysts were determined by using a Micromeritics ASAP-2020 sorptometer apparatus. Before the measurement of BET, the samples were degassed at 350 °C for at least 5 h under vacuum. The total surface area was calculated according to the BET method.

Hydrogen temperature programmed reduction (H₂-TPR) experiments of the calcined Pd/SiO₂/COR catalysts were carried out on a Thermo Electron TPD/R/O 1100 series instrument equipped with a thermal conductivity detector (TCD). The samples were reduced in a stream of 10% H₂ flow (volume fraction, balanced by Ar) with the flowrate of 30 mL·min⁻¹ and heating rate of 10 K·min⁻¹ from 273 to 1173 K.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) experiments of the calcined Pd/SiO₂/COR catalysts were performed on a Shimadzu Corporation-ICP-7500.

X-ray photoelectron spectroscopy (XPS) spectra were performed on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific, USA). XPS spectra were recorded using monochromated Al K α excitation at pass energies of 200 eV for survey and

30 eV for high-resolution scans. The binding energy calibration of all spectra was referenced to the adventitious carbon (C1s) signal at 284.6 eV to reduce the charging effect of samples.

2.3. Catalytic activity measurement Pd/SiO₂/COR

The catalytic hydrogenation of eAQ was performed in a stainless steel fixed-bed reactor (20 mm in inner diameter and 450 mm in length) with a central thermocouple to measure the temperature of reaction zone under atmospheric pressure. There are 11 elements of Pd/SiO₂/COR monolith catalysts packed in the constant temperature zone of the reactor and embedded between the pretreated cordierite supports in both sides of the reaction zone to support the catalyst bed. The 11 elements were tightly installed so that the gaps between each other, as well as between monolith section and stainless steel tube, can be ignored. Before the hydrogenation experiments, the catalysts were reduced in situ under hydrogen atmosphere at 150 °C, and then the reactor was cooled down to the reaction temperature. The feedstock (eAQ dissolved in C9 aromatics and trioctyl phosphate mixture with a volume ratio of 3:1, the concentration of eAQ solution was 60 g·L⁻¹) was then pumped into the reactor by double-plunger pump, while hydrogen was input through a gas mass flow meter. Then, the hydrogenated anthraquinone working solution was pumped into the oxidation device for oxidation reaction by the air from oil-free air generator (GC-ready SPB-5000 Automatic Air Source) to produce H₂O₂ at room temperature. Afterwards, the oxidated working solution (H₂O₂ solution) was extracted with 25.2 wt% sulfuric acid solution several times.

The content of H₂O₂ obtained from the oxidation of eAQH₂ was measured by the KMnO₄ titration. The yield of H₂O₂ ((H₂O₂(mol)/EAQ(mol)) · 100%) and the space time yield (STY, (H₂O₂(g)/Pd(g))/time(h)) were introduced to characterize the catalytic performance of Pd/SiO₂/COR catalysts with different Pd contents.

3. Results and discussion

3.1. Characterization of monolith catalysts

3.1.1. XRD analysis

Fig. 1 shows the XRD patterns of the cordierite (COR), the pretreated COR, the SiO₂/COR, and the Pd/SiO₂/COR monolith catalysts

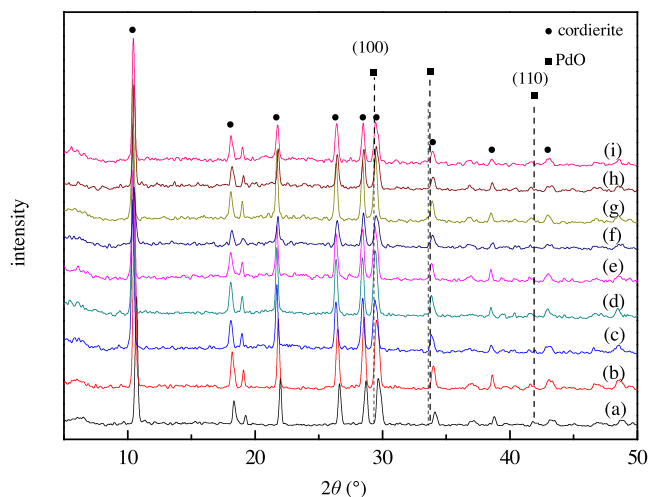


Fig. 1. XRD patterns of Pd/SiO₂/COR samples with various contents of Pd. (a) COR; (b) pretreated COR; (c) SiO₂/COR; (d) 0.6% Pd/SiO₂/COR; (e) 1.0% Pd/SiO₂/COR; (f) 1.2% Pd/SiO₂/COR; (g) 1.5% Pd/SiO₂/COR; (h) 1.7% Pd/SiO₂/COR; (i) 2.2% Pd/SiO₂/COR.

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