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Cumene hydroperoxide hydrogenation over Pd/C catalysts

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ABSTRACT

Pd/C catalysts were prepared by wet impregnation using K_2PdCl_4 as precursor and their performance in hydrogenation of cumene hydroperoxide (CHP) was investigated. The catalytic activity was examined on the formaldehyde-reduced and on the hydrogen-reduced Pd/C catalysts. Results from XRD, TEM and CO chemisorption showed that reduction methods have a significant impact on the palladium particles size of resulting catalysts. Formaldehyde-reduced Pd/C catalyst has larger palladium particles than hydrogen-reduced Pd/C catalyst. Consequently, higher activity but lower selectivity to α-cumyl alcohol (CA) was obtained on formaldehyde-reduced Pd/C catalyst. Moreover, hydrogenation of CHP over hydrogen-reduced Pd/C catalyst can give similar CA selectivity to Na_2SO_3 reduction process, an industrial process for CA production. High rate of CHP conversion and CA selectivity can be obtained at an elevated temperature and H_2 pressure. Kinetics studies revealed that CHP hydrogenation is zero-order for CHP concentration and the activation energy was calculated to be 13.6 kJ/mol.

1. Introduction

Cumene hydroperoxide (CHP), a kind of typical organic peroxide, posses a potential hazard owing to its relatively weak oxygen–oxygen linkage. It may result in fire or explosion when it contacts with heat, acids, bases, metal, contaminants, etc. [1]. Besides the major application in producing phenol and acetone [2–4], CHP is also a source material for producing dicumyl peroxide (DCP). In the process of DCP production, CHP is catalyzed by dilute about 45 wt% NaOH [1] or reduced by sodium sulfite (Na_2SO_3) solution [5] to yield α-cumyl alcohol (CA). Both of them have the problem of pollution. As a more economical and environmental technology, catalytic hydrogenation of CHP to CA with the aid of a catalyst is promising.

In the field of fine chemical, especially in the hydrogenation process, carbon supported palladium catalysts (Pd/C) are the most widely used hydrogenation catalysts both in research laboratories of academia and the chemical industry [6]. Although many organic groups, such as C—X, C═C, C—O, C═O, can be hydrogenated over Pd/C catalysts, few studies on hydrogenation of hydroperoxides were reported. For example, Il'ina et al. [7] reported that pinanol can be prepared with high selectivity by the hydrogenation of pinane hydroperoxide on a Pd/C catalyst under mild conditions.

In this paper, hydrogenation of CHP was performed in a fix-bed reactor, using Pd/C catalyst with low Pd loading. The purpose of this study was to address: (i) comparing the performance of hydrogen reduction with Na_2SO_3 reduction; (ii) establishing the reduction method for Pd/C catalyst; (iii) establishing the reaction order and activation energy of CHP hydrogenation. Moreover, the catalysts were characterized by BET, CO chemisorption, XRD and TEM to correlate the physicochemical properties to the catalytic performance.

2. Experimental

2.1. Chemicals

CHP was obtained from Shanghai Gaoqiao Company, SINOPEC. The composition of the feedstock and product reduced by Na_2SO_3 is reported in Table 1. The other reagents, such as $PdCl_2$, KCl, $Na_2S_2SO_3$, KI, glacial acetic acid and formaldehyde were analytical grade and were supplied by Sinopharm Chemical Reagent Co., Ltd. Activated carbon was purchased from Shanghai Activated Carbon Co., Ltd. and treated by 35 wt% HNO_3 at 60 °C before utilization. Water used in the reaction was deionized. The purities of hydrogen used in the experiments were more than 99.99%.

2.2. Catalyst preparation

Pd/C catalysts used in the experiments were prepared by wet impregnation using K_2PdCl_4 (prepared from $PdCl_2$ and KCl) as precursor. Following impregnation, the sample was divided into two parts; one was directly reduced by formaldehyde at 80 °C with vigorous stirring. After reduction, the sample was washed by deionized water for several times and then dried in an oven at 120 °C for 2 h,

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Table 1
Composition of CHP feedstock and product distribution of CHP reduced by Na_2SO_3.

Entry	Composition (mol%)				
	CHP	Cumene	CA	AP	α-MS
Feedstock	44.1	55.3	0	0.6	0
[a]Product	0	52.2	46.6	0.8	0.4

[a] Data from CA unit in Shanghai Gaoqiao Company Refinery Plant.

and the resulting catalyst was referred as Pd/C(FR). The other part was dried in an oven at 120 °C for 2 h and reduced in flowing hydrogen at 300 °C for 3 h; the resulting catalyst was referred as Pd/C(HR). The final Pd loadings of the Pd/C catalysts are determined using ICP-AES to be approximate 0.5 wt%.

2.3. Catalyst characterization

The specific surface area of the different catalysts was determined by nitrogen adsorption at −77 °C, according to the BET method using Micrometrics ASAP2010 apparatus.

Palladium dispersion was measured by CO chemisorption on a Micrometrics AutoChem II 2920 apparatus at room temperature, using a thermal conductivity detector (TCD) to monitor CO consumption and assuming a CO:Pd = 1:1 stoichiometric ratio. Prior to chemisorption, the catalyst was reduced in flowing hydrogen at 300 °C for 2 h and then treated in flowing helium for 1 h.

X-ray powder diffraction (XRD) patterns of all catalysts were recorded on a Rigaku D/Max 2550VB/PC X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 0.15406 nm) with a scan range of 10–80° at 40 kV and 100 mA. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File.

TEM images of reduced catalysts were obtained on a JOEL JEM 2010 apparatus. Prior to observation, the catalysts were abraded to fine powder and then collected on holey carbon films supported on Cu grids by placing a few droplets of a suspension of the ground samples in alcohol on the grids, followed by drying at ambient conditions. The size distribution of all catalysts was determined by observing several areas of the grid. Several hundred particles visible on the micrographs were counted and the average value of palladium particle size was calculated by the following equation:

$$\bar{d} = \frac{\sum n_i d_i}{\sum n_i} \quad (1)$$

where n_i is the number of particles of diameter d_i.

2.4. Catalytic activity test

Liquid phase hydrogenation of CHP was preformed in a vertical fixed-bed, continuous down-flow stainless micro-reactor (i.d. 8 mm, length 400 mm, Fig. 1) with a jacket. In a typical run, 0.5 g catalyst was diluted with 10 ml quartz sand (treated by strong hydrochloric acid and calcined in air at 700 °C for 3 h) and packed at the centre of the reactor. Moreover, one plug of quartz wool was used at the bottom of the reactor to avoid the leaching of catalyst. The reaction system was flushed with hydrogen gas and the system pressure was controlled by a back-pressure regulator. The temperature was maintained through a circulating constant temperature bath. After the desired reaction pressure and temperature were attained, CHP in cumene solution was pumped into the reactor at a flow rate of 0.15 ml/min while hydrogen gas was at a flow rate of 90 ml/min.

2.5. Product analysis

The conversion of CHP was measured by iodimetry and the hydrogenation products were analyzed using a gas chromatography (HP-6890) with a flame ionization detector (FID) and a 30.0 m × 32 mm × 0.3 μm capillary column (HP-1). The injection temperature and detect temperature were both at 200 °C with a temperature programmed from 100 to 200 °C at a ramp temperature rate of 10 °C/min.

CHP conversion and CA selectivity were calculated using the following equations:

$$\text{CHP conversion}\,[\%] = \frac{\text{Initial CHP}\,[\text{wt.\%}] - \text{Final CHP}\,[\text{wt.\%}]}{\text{Initial CHP}\,[\text{wt.\%}]} \times 100\% \quad (2)$$

$$\text{CA selectivity}\,[\text{mol\%}] = \frac{\text{CA}\,[\text{mol\%}]}{\text{Initial CHP[mol\%]} - \text{Final CHP[mol\%]}} \times 100\% \quad (3)$$

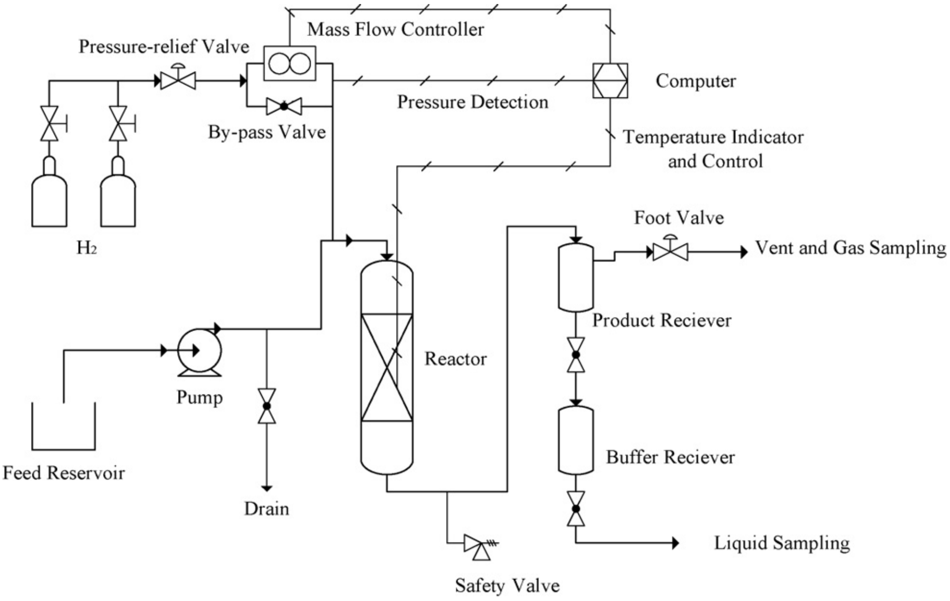

Fig. 1. Catalytic test apparatus.