



Acidic Montmorillonite/Cordierite Monolithic Catalysts for Cleavage of Cumene Hydroperoxide[☆]



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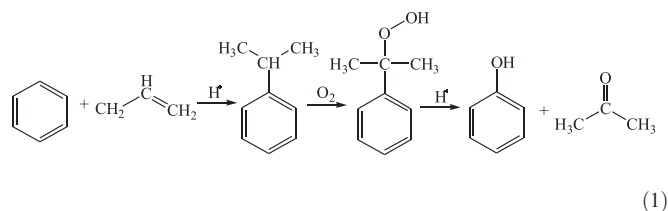
ABSTRACT

In this work, a series of acidic montmorillonite/cordierite monolithic catalysts were prepared by a coating method using silica sol as the binder. The morphology and structure of the acidic montmorillonite/cordierite samples were characterized by means of X-ray diffraction (XRD), N₂ adsorption/desorption isotherms, and scanning electron microscope (SEM). The cleavage of cumene hydroperoxide (CHP) in a conventional fixed-bed reactor was chosen as a model reaction to evaluate the catalytic activity of the monolithic catalysts. The influences of acidic montmorillonite loading, reaction temperature, CHP concentration, and weight hourly space velocity (WHSV) on the catalytic activity and selectivity of phenol were studied. The results indicated that the obtained acidic montmorillonite/cordierite monolithic catalysts were firm and compact, and the loading of acidic montmorillonite was found to reach 40% (by mass) after three coating operations. The surface area of acidic montmorillonite/cordierite catalysts increases greatly as acidic montmorillonite loading increases due to higher surface area of acidic montmorillonite. Under the optimal reaction conditions (acidic montmorillonite loading of 32.5% (by mass), temperature of 80 °C, a mass ratio of CHP to acetone of 1: 3, and WHSV of CHP of 90 h⁻¹), the conversion of CHP can reach 100%, and the selectivity of phenol is up to 99.8%.

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1. Introduction

Both phenol and acetone are important chemicals in the organic chemical industry. The cumene peroxidation method for the preparation of phenol and acetone is the most important technology in the current world [1], which was first developed in the 1950s. The process consists of the following three steps: (1) cumene generation by alkylation of benzene with propylene, (2) cumene oxidization by oxygen to cumene hydroperoxide (CHP), and (3) CHP cleavage over acid catalysts to phenol and acetone [2–4]. The following reaction presents this process:



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Among these processes, CHP cleavage has an important impact on the yield of the product. The commercial acid catalyst most commonly used for CHP cleavage is concentrated sulfuric acid. However the concentrated sulfuric acid shows intrinsic disadvantages including: (1) less selectivity and more byproducts [5]; (2) serious equipment erosion due to addition of inorganic or organic alkali for neutralization; (3) the addition of alkali makes the subsequent operation complicated and the distillation column life cycle shortened; (4) phenol-containing waste water is produced due to added solvent water, leading to environmental pollution [6].

In the recent two decades, solid acid catalysts were extensively studied due to the possibility to avoid the disadvantages of the traditional process. The solid acid catalysts consist of acid resin, zeolite, acidic montmorillonite, metallic oxide, heteropoly acid, loaded L acid, etc. [7]. Among these catalysts, acidic montmorillonite and acid resins exhibit appropriate catalytic performance [8]. The ion-exchange resin catalyst was proposed in the industry to catalyze CHP cleavage to produce phenol [9,10]. However, the fragmentation, instability, easy erosion and nonuniform distribution of acidic center are the main disadvantages for these solid acid catalysts, which restrict their wide industrial application. Therefore, it is necessary to develop new and appropriate acidic catalysts to replace solid acid catalysts.

At present, the monolithic catalyst as a novel kind of catalyst with the internal structure of a regular honeycomb structure exhibits

some advantages compared with the conventional particulate catalyst, e.g., low pressure drop, high effectiveness factor, minimum axial dispersion stemming from the uniquely structured multichannel configuration, high catalyst utilization efficiency and good heat and mass transfer performances [11–14]. Moreover, the monolithic structures are beneficial to improve the surface area per unit of bed volume, which is conducive to timely access of the reactants and timely discharge of the products so as to intensify the chemical reaction process. In addition, it is convenient to install or uninstall the monolithic catalyst into or out of the reactor and also easy for the maintenance, resulting in low operational cost [15–17]. CHP cleavage is a strong exothermic reaction and there even exists the danger of explosion. A fast and effective removal of reaction heat is absolutely necessary for the process. The typical method of heat removal is by acetone evaporation. The low bed pressure drop of monolithic catalysts is conducive to heat transfer so as to reduce the formation of byproducts and improve the selectivity. Currently, monolithic catalysts have been applied to plenty of catalytic reactions, e.g., the catalytic combustion and the catalytic oxidation [18], the methane steam reforming [19], the hydrogenation dehydrogenation reaction [20] and the Fischer–Tropsch synthesis [21], and exhibit excellent catalytic performances. Most monolithic catalysts adopt the cordierite as substrate due to its excellent thermal stability, small thermal expansion coefficient and impact resistance [22–24]. Because the specific surface area of cordierite is very small, the intermediate coating usually is loaded firstly and then the active component is coated, thus the preparation technology is more complicated. Thus, the one-step coating method of preparing monolithic catalysts is simple, easy to operate and in favor of industrial production.

In this work, the one-step coating method was used to prepare a series of acidic montmorillonite/cordierite monolithic catalysts, and then the samples were characterized by X-ray diffraction (XRD), N_2 adsorption/desorption and scanning electron microscope (SEM) to characterize the morphology and structure of catalysts. The catalytic performance of the catalysts for the cleavage of cumene hydroperoxide was evaluated in a fixed-bed reactor. The influences of acidic montmorillonite loading, reaction temperature, CHP concentration, and WHSV of CHP on the conversion of CHP and selectivity of phenol were studied. Finally the optimum operation conditions were obtained.

2. Experimental

2.1. Materials

Cordierite monolith support (31 cells per square centimetre, hole size: 2 mm × 2 mm, surface roughness: ~4.0 μm) was purchased from Beijing Chuangdaoofu Fine Ceramics Co. Amberlyst 15 (concentration of acid sites $\geq 4.7 \text{ mol} \cdot \text{kg}^{-1}$, surface area: $40 \text{ m}^2 \cdot \text{g}^{-1}$, pore volume: $0.4 \text{ cm}^3 \cdot \text{g}^{-1}$, pore size: 25 nm) was provided by Aoyang Chemical Engineering Co., Zhangjiagang, Jiangsu. CHP [about 80% (by mass) in cumene] was obtained from Yanshan Petrochemical Co., Beijing. Other chemicals and reagents such as sulfuric acid, montmorillonite (neutral, average particle size: 10.0 μm, specific surface area: $32.1 \text{ m}^2 \cdot \text{g}^{-1}$), silica sol [aqueous dispersion of 30% (by mass) of nano SiO_2], oxalic acid and acetone were of analytical grade and supplied by Tianjin Guangfu Fine Chemical Research Institute without further purification.

2.2. Preparation of catalysts

The montmorillonite powder was activated using 30% (by mass) sulfuric acid, heated at 100 °C for 4 h, and then washed with deionized water repeatedly till pH ≥ 4 , and finally the acidic montmorillonite was dried in an oven. The acidic montmorillonite, silica sol [30% (by mass) dispersion], and deionized water were mixed together at a certain proportion (mass ratio of acidic montmorillonite:silica sol:deionized water being 1:1.5:2), then the mixture was stirred on a magnetic stirring apparatus at room temperature for 3 h, and the pH value was kept at

3.0 by addition of dilute nitric acid when needed so as to obtain the active slurry.

The cordierite samples with a diameter of 8 mm and length of 20 mm were cut from a commercial honeycomb cordierite with a cell density of 31 cpsc (cells per square centimetre). The samples were pretreated using 20% (by mass) oxalic acid solution boiling for 2 h and then washed with deionized water. Afterwards, these cordierite samples were calcined in a muffle furnace at the temperature of 550 °C for 4 h to remove the absorbed impurities. The dried cordierite monolith sample was dipped into the active slurry obtained above for 5 min, and the excess slurry in the monolith channels was removed with compressed air, and then dried horizontally in air at 120 °C for 30 min. The coating procedure was repeated 1–5 times to achieve the expected loading of 13.0%–38.5% (by mass). Afterward, the monolithic catalysts were calcined in air at 550 °C for 4 h. Some properties of the prepared monolithic catalysts were listed in Table 1.

2.3. Characterization of catalysts

The adhesion degree of acidic montmorillonite coated onto the monolith cordierite support was measured by an ultrasonic method. Five monolithic catalysts of different acidic montmorillonite loadings were submerged in five beakers containing alcohol, and then beakers are placed in an ultrasonic oscillator containing water. With ultrasonic power of 160 W of 25 kHz exerted for 60 min, the mass loss of the coating was less than 3% (expulsion rate in Table 1).

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advanced diffractometer, with Ni detector side filtered $\text{Cu-K}\alpha$ radiation over a 2θ range from 5° to 50° at 40 kV and 40 mA using a step size of 5° and a step time of 1 min.

Scanning electron microscopy (SEM) micrographs were recorded on a JEOL JSM-6701F microscope working at 5.0 kV accelerating voltage. Before observation, the sample was sprayed with gold by an ion sputtering instrument in order to make the sample conductive.

The BET surface area, pore volume and pore size distribution were determined by using a Micromeritics ASAP-2020 surface area analyzer. Before each adsorption/desorption, the samples were degassed for at least 5 h at 350 °C under vacuum. Surface area was calculated with the BET equation, while pore volume and pore size distribution were obtained using the BJH method.

2.4. Catalytic activity measurements

Catalytic activity was measured using a conventional fixed-bed reactor apparatus (8 mm in inner diameter and 300 mm in length packed with 5 cylindrical monolithic catalysts above) at atmospheric pressure. A schematic diagram of the experimental apparatus is shown in Fig. 1. Five monolithic catalysts were placed in the reaction tube, separated by quartz sand and quartz wool, and the reaction temperature was maintained at 60 °C–90 °C by a water bath.

In the comparison experiment, the acid resins (Amberlyst 15) and five monolithic units (mass of each unit is 1.4 g and the acidic montmorillonite loading is 32.5%, by mass) were placed in the reactor. 2.275 g acid resin (Amberlyst 15, dried at 80 °C for 24 h before use), an equal amount to the acidic montmorillonite on the five monolithic units, mixed with 0.45 mm–0.8 mm glass beads uniformly was placed in the

Table 1
Properties of monolithic catalyst

Coating times	Loading/% (by mass)	Thickness of coating/mm	Expulsion rate/%
1	13.0	0.083	0.8
2	19.5	0.114	1.1
3	25.8	0.155	1.7
4	32.5	0.196	2.2
5	38.5	0.231	2.9

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