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Influence of ceria promoter on shell-powder-supported Pd catalyst for the complete oxidation of benzene

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ABSTRACT

Pearl shells are the main waste of the pearl industry, which discards millions of tons of pearl shells each year in China. To date, the use of pearl shells in the complete oxidation of volatile organic compounds (VOCs) has not been reported. In this paper, shell powder (SP) was used as a carrier for ceria and Pd catalysts for the complete oxidation of benzene. The influence of the ceria promoter on the texture/structure and catalytic performance of Pd/SP was investigated. The results show that adding ceria into the SP support increased the BET surface area and total pore volume and decreased the sinterability of SP. The catalytic activity and H_2 temperature-programmed reduction (H_2-TPR) results show that adding ceria can greatly improve the oxidation properties of Pd/SP catalysts and enhance the catalytic activity for the complete oxidation of benzene. The improvement in the catalytic activity is mainly due to the optimization of the catalyst texture/structure and redox properties by the strong interaction of Pd and ceria and the addition of ceria.

1. Introduction

Volatile organic compounds (VOCs) have a high vapor pressure and low water solubility and are recognized as major contributors to air pollution both directly and as precursors to ozone and photochemical smog. The most efficient methods for VOC destruction are thermal and catalytic incineration, with the latter being the most popular because it is often more versatile and economical for low concentrations of organic emissions [1,2]. Both classes of catalysts, noble metals and transition metal oxides, have been widely studied for use in the destruction of halogenated and non-halogenated compounds [3–7]. Noble-metal-based catalysts, despite their higher costs, are preferred because of their high specific activity, resistance to deactivation and regeneration ability [2].

Although noble metals (Pd or Pt) are highly active in catalytic oxidation, they are also easily sintered and poisoned at relatively low temperatures, causing catalyst deactivation [8]. Ceria can act as a promoter and a reducible support. Its unique ability to store and release oxygen (redox property) makes it attractive for oxide catalysts because it can provide lattice oxygen and prevent the sintering of noble metals [9,10]. The redox property of ceria leads to oxygen vacancies, resulting in high oxygen storage capacity. This feature improves the thermal resistance of the supports, the dispersion of supported metals and the oxidation and reduction of supported noble metals and hinders coke formation on the catalyst surface [11–16]. Ceria has excellent thermal and mechanical resistance [17] and increases the thermal stability of the support [16].

Supports are an important component of Pd-loaded catalysts, often profoundly affecting the generation of active species and the catalytic performance [18,19]. Different types of supports, such as porous materials, alumina and silica, are comprehensively investigated in hydrocarbon catalytic oxidation [20–23]. Pearl shells are the main waste of the pearl industry, which discards millions of tons of pearl shells each year in China. The disposal of pearl shell waste from shellfish farms is a serious problem; the waste is often left untreated for a long time in the field, producing a foul odor. To reduce the amount of oyster shell waste, researchers have investigated its use as a construction material [24], a stabilizer of acid sulfate soil [25] and a phosphate adsorbent [26]. To the best of our knowledge, the application of pearl shell (shell powder) in the complete oxidation of VOCs has yet to be reported. Such a study could be of interest to the many countries that would benefit from a way to utilize waste from the pearl industry. Pearl shells are a biogenic hybrid composite consisting of alternating layers of calcium carbonate tablets (~95%, 5–20 μm in width and 0.5–1.0 μm in thickness) and 30–50 nm layers of elastic biopolymers [27–29]. High calcination temperatures accelerated the degradation of the hydrophobic biomacromolecules, producing the porous particle surface of hydrophilic calcium carbonate [29]. We demonstrate that such a material with a ceria promoter can be effectively applied as a carrier in VOC catalytic oxidation.

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The objective of this paper is to demonstrate that shell powders (SPs) can be used as a carrier in the complete oxidation of benzene. SP-supported Ce and Pd catalysts were synthesized, and their catalytic performance in the complete oxidation of benzene was studied. The effect of the addition of ceria on the texture and structure of SP was also investigated. The supports and catalysts were characterized by X-ray powder diffraction (XRD), N_2 adsorption, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and H_2 temperature-programmed reduction (H_2-TPR) techniques.

2. Experimental

2.1. Materials

Pearl shells were obtained from Zhuji Pearl Shell Farm (Zhuji, Zhejiang, China). $Ce(NO_3)_3{\cdot}6H_2O$ was obtained from the National Engineering Research Centre of Rare Earth Metallurgy and Functional Materials (Baotou, Neimenggu, China). H_2PdCl_4 was obtained from Shanghai Chemical Reagents Factory. All reagents were of reagent grade and used as received.

2.2. Support and catalyst preparation

The pearl shells were washed with tap water to remove sand and seaweed deposited on the shell surface and then dried naturally. The shells were crushed roughly into powder using a ball mill (QM-3SP04, Nanjing, China) with a 200 mesh sieve. The shell powders (SPs) were then dried at 110 °C for 3 h and stored in a desiccator. The SP (40–60 mesh) dried at 500 °C for 2 h is labeled SP (500).

Ce/SP (500) was prepared by impregnation with an aqueous solution of 1.0 M Ce $(NO_3)_3{\cdot}6H_2O$. The impregnated samples were kept for 12 h at room temperature. Next, the samples were dried at 110 °C, and calcined at 500 °C for 1 h. The Ce contents were 2, 4, 6 and 8 wt.%.

Pd/SP (500) and Pd/Ce/SP (500) were prepared by impregnation with a 10 mg/ml aqueous H_2PdCl_4 solution as the metal precursor. The impregnated samples were reduced by hydrazine hydrate and then filtered and washed with a large amount of deionized water until free of chlorides. The samples were then dried at 110 °C and calcinated at 400 °C for 2 h. The Pd content for all catalysts was 0.2 wt.%.

2.3. Catalyst activity determination

Prior to the catalytic tests, the samples were pretreated for 1 h in air at 500 °C. Benzene oxidation was carried out in a micro reactor (quartz glass; 6 mm i.d., 8 mm o.d., WFS-3010, Xianquan, Tianjin, China) under atmospheric pressure at a space velocity of 20,000 h^{-1}. The reactive flow (125 ml/min) was composed of air and gaseous benzene (1000 ppm). The catalyst was loaded in the quartz reactor with quartz wool packed at both ends of the catalyst bed, and the bed volume was approximately 0.375 ml. A thermocouple was placed in the center of the catalyst bed to record the reaction temperature and control the furnace. Benzene conversion in the effluent gas was analyzed by on-line gas chromatography (Shimadzu, GC-14C). Only CO_2 and H_2O were detected by mass spectrometry (QIC-20, HIDEN). Thus, the conversion was calculated based on benzene consumption.

2.4. Catalyst characterization

X-ray diffraction (XRD) was performed on a Rigaku D/max2550PC instrument. The diffraction patterns were recorded with Cu Kα radiation (300 mA, 40 kV). The average $CaCO_3$ and CeO_2 crystallite sizes were calculated by the Scherrer equation using the width at half height of the line profiles corresponding to the (1 0 4 or 1 1 1) and (1 1 1) crystal planes, respectively. The XRD identification is supported by the JCPDS-ICDD cards corresponding to the different phases.

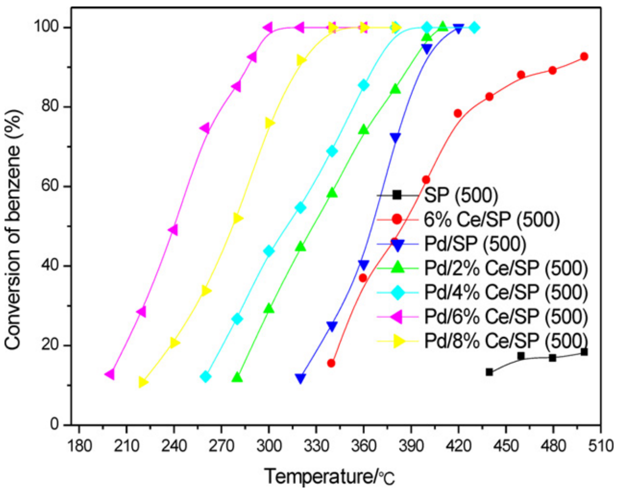

Fig. 1. Temperature dependence of benzene conversion over the catalysts: effect of adding ceria on Pd/SP (500).

The BET surface area (S_{BET}), total pore volume (D_v) and pore diameter (d_c) of the samples were obtained from the N_2 adsorption isotherms at −195.8 °C using a Tristar II3020 apparatus (Micromeritics, USA). Prior to the adsorption measurements, the samples were outgassed at 250 °C under vacuum for 4 h.

The morphology and size of the particles were observed using SEM (S-570, Hitachi, Japan). EDS analysis was performed on an Environmental SEM instrument (Quanta 200, FEI, USA) with an energy dispersive system (EDS, IE350MT) to obtain the elemental content of the metal phase of the catalyst.

The palladium content was determined by inductively coupled plasma (ICP) after the dissolution of the catalysts in a mixture of HF and HNO_3 solution. The result shows that the palladium content is approximately 0.2 wt.% for all the studied catalysts.

H_2 temperature-programmed reduction (H_2-TPR) measurements were carried out on CHEMBET-3000 (Quantachrome, USA) instrument to observe the reducibility of the catalysts. Prior to H_2-TPR measurement, 50 mg of the catalyst was pretreated at 300 °C in air for 0.5 h, after which the temperature was decreased to −30 °C.

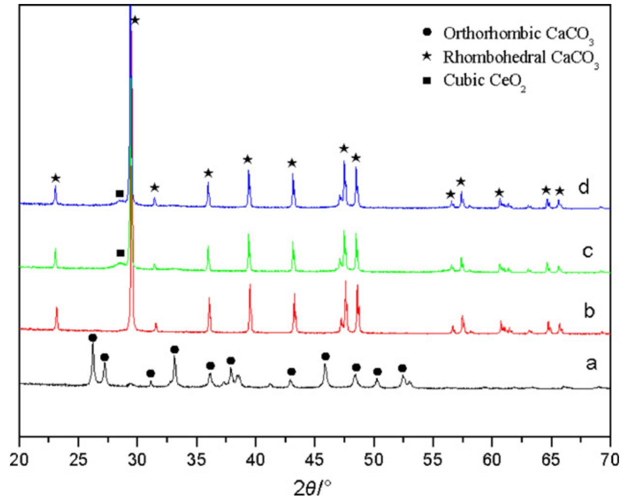

Fig. 2. XRD patterns of the catalysts between 20° and 70°: (a) SP; (b) SP (500); (c) 6%Ce/SP (500); (d) Pd/6%Ce/SP (500).