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Selective oxidation of toluene over the new catalyst cobalt tetra (4-hydroxyl) phenylporphyrin supported on zinc oxide

Guan Huang *, Feng Xiang, Tian-Ming Li, Yue-Xiu Jiang, Yong-An Guo

Guangxi Key Lab of Petrochemical Resource Processing and Process Intensification Technology, College of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

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ABSTRACT

Cobalt tetra(4-hydroxyl)phenylporphyrin/ZnO was prepared and used for the catalytic oxidation of toluene with O_2. Its activity has been increased by 70% over that of the cobalt tetra(4-hydroxyl)phenylporphyrin and the effective reuse of the supported catalyst for toluene oxidation is seven times per 1 mg (1.35×10^{-6} mol) cobalt tetra(4-hydroxyl)phenylporphyrin, demonstrating the promotion by zinc oxide.

1. Introduction

Selective catalytic oxidation of hydrocarbons using an environmentally friendly and clean production method is very desirable. Although good performance for the oxidation of toluene to benzaldehyde, benzyl alcohol and bezoic acid in good yield [1–9] is observed, the need to use noble metals and additives restricts wide application. Even if a traditional method, such as the chlorination of toluene followed by hydrolysis [10], was temporarily employed, this represents a seriously polluting process. Therefore, selective catalytic oxidation of toluene to bezaldehyde, benzalcohol and benzoic acid still remains a major challenge.

During past decades, some methods of using biomimetic catalysts for the selective oxidation of toluene have been reported [11–13]. Although the catalytic efficiencies for the biomimetic catalysts did not lead to sufficiently high yields for industrial production, some green catalysts have shown promise in terms of increases in activity and lifetime compared with non-green catalysts and the corresponding methods. Metalloporphyrins, as typical in homogeneous catalytic systems, have a common fatal shortcoming, which is that they are easily oxidized and hence degraded by O_2. This can be overcome by various methods of immobilization of the metalloporphyrin on to organic, inorganic and hybrid supports. Previously, Co TPP/CTS was used for the catalytic oxidation of toluene to produce benzaldehyde and benzyl alcohol. The catalytic activity of Co TPP can be promoted by chitosan. However, on average, a quantity of catalyst containing only 1 mg (1.5×10^{-6} mol) Co TPP supported on chitosan can be reused only once because the chitosan is burned out in the oxidation process [14]. This suggested that we use zinc oxide as the support, immobilizing the cobalt tetra (4-hydroxyl) phenylporphyrin. In addition, we explore the relationship between the stability of zinc oxide when exposed to high temperature and the protection of cobalt tetra (4-hydroxyl) phenylporphyrin from destruction by O_2. This may promote the catalytic activity of the Co porphyrin by zinc oxide and provide a better understanding of the effect of the support on the catalytic performance of metal porphyrins.

2. Experimental

2.1. Instruments and reagents

UV–vis spectra were recorded on a Perkin-Elmer L-17 spectrometer. FT-IR spectra were recorded on a Perkin-Elmer model 783 IR spectrophotometer. GC analysis of the catalytic oxidation products was accomplished with a Shimadzu GC-16A chromatograph equipped with a 30 m × 0.32 mm × 0.5 μm FFAP capillary column and a flame ionization detector. The reactor was a KCF-10 250-ml autoclave fitted with a magnetic stirrer and a CYS-1 digital oxygen meter. All reagents and solvents were of analytical grade and were obtained commercially. Cobalt tetra (4-hydroxyl) phenylporphyrin [Co THPP] was prepared according to published procedures [15–18]. No impurities were found in the toluene by GC analysis before use.

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* Corresponding author. Tel.: +86 771 3237868; fax: +86 771 2851043.
E-mail address: huangg66@126.com (G. Huang).

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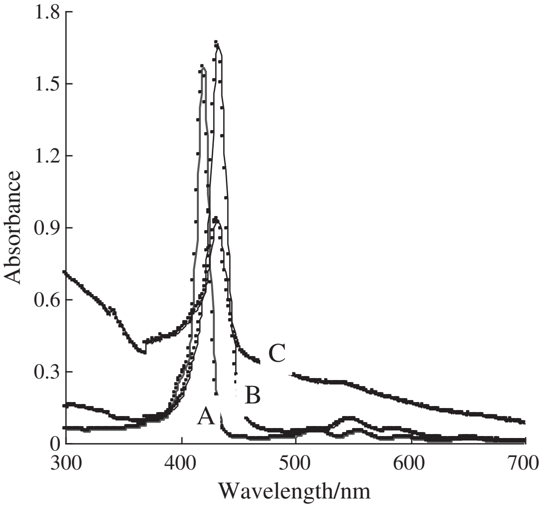

Fig. 1. UV–Vis spectra at room temperature. (A) Ethanol solution of H_2 THPP. (B) Ethanol solution of Co THPP. (C) Suspension of Co THPP/ZnO in ethanol.

2.2. Preparation and analysis of zinc oxide-supported Co THPP

Under stirring, 0.25 mol of zinc sulfate heptahydrate ($ZnSO_4$7H2O) was dissolved in distilled water, and 0.50 mol of NaOH as precipitation agent was added to pH = 8. The white zinc hydroxide precipitate that formed was filtered and washed with distilled water until no SO_4^- ion was detected. Then the precipitate was added to 100 ml of ethanol in a three-neck flask with stirring at high speed for 0.5 h. Subsequently, 30 mg of Co THPP dissolved in 20 ml of absolute ethanol was slowly added to the above suspension, and the mixture was heated to 65 °C with rapid stirring for 5 h. The shallow red suspension was filtered and washed with bulk distilled water and the pink cake was dried at 0.09 MPa and 160 °C for 5 h. As a result, 19.6 g of the pink supported catalyst, Co THPP/ZnO, was obtained. The amount of Co THPP supported per gram of ZnO was 2.0×10^{-6} mol, as determined by UV–vis spectrophotometry [19].

2.3. Toluene oxidation over Co THPP/ZnO with O_2

Into a 500-ml autoclave reactor were added a measured amount of Co THPP/ZnO and 200 ml of toluene. The mixture was stirred at 300 rpm and heated to 180 °C. Then O_2 was continuously pumped into the reaction system and the pressure was kept at 0.5 MPa. The flow of oxygen was measured with a rotameter, and the oxygen concentration of the tail gas was determined with a CYS-1 digital oxygen detector. Samples of the reaction mixture were identified by GC–MS and were quantified by GC using an internal standard method with nitrobenzene as the standard substance. The GC analysis for benzaldehyde and benzylalcohol was carried out as follows: N_2 was used as the carrier gas, at a flow rate of 50 mL/min; the column temperature was 140 °C; the injector temperature was 160 °C; and the detector temperature was 180 °C. Benzoic acid and its ester were measured according to a documented procedure [20]. To study subsequent reuse of the Co THPP/ZnO catalyst, the most recently used catalyst was separated from the reaction mixture, naturally dried at R. T., and then put into the next catalytic toluene oxidation.

3. Results and discussion

3.1. Characterization of Co THPP/ZnO material

Meso–tetra (4-hydroxyl) phenylporphyrin[H_2 THPP] and its cobalt porphyrin [Co THPP] were synthesized according to the literature method as above. Both are soluble in ethanol. The absorption spectra of H_2 THPP and Co THPP at a room temperature showed peaks at 420 nm (Soret peak), 518 nm, 556 nm, 594 nm, 651 nm (Q peaks) and 433 nm (Soret peak), 549 nm, 588 nm, 643 nm (Q peaks), respectively, as shown in Fig. 1 (A and B). Co THPP was immobilized on white zinc hydroxide and subsequently, after filtering the suspension and drying the cake at 160 °C and 0.09 MPa, the pink Co THPP/ZnO material was obtained. This indicates the presence of Co THPP on the ZnO support. This was also confirmed by UV–vis spectroscopy for the supported catalyst. The spectra for Co THPP/ZnO in ethanol suspension are shown in Fig. 1C. In the ethanol solution of Co THPP (Fig. 1B) a Soret peak was visible at 433 nm. After immobilization of Co THPP on ZnO, no significant red shift in the Soret peak position was observed in the UV–vis spectrum (Fig. 1C), indicating that the porphyrin ring was

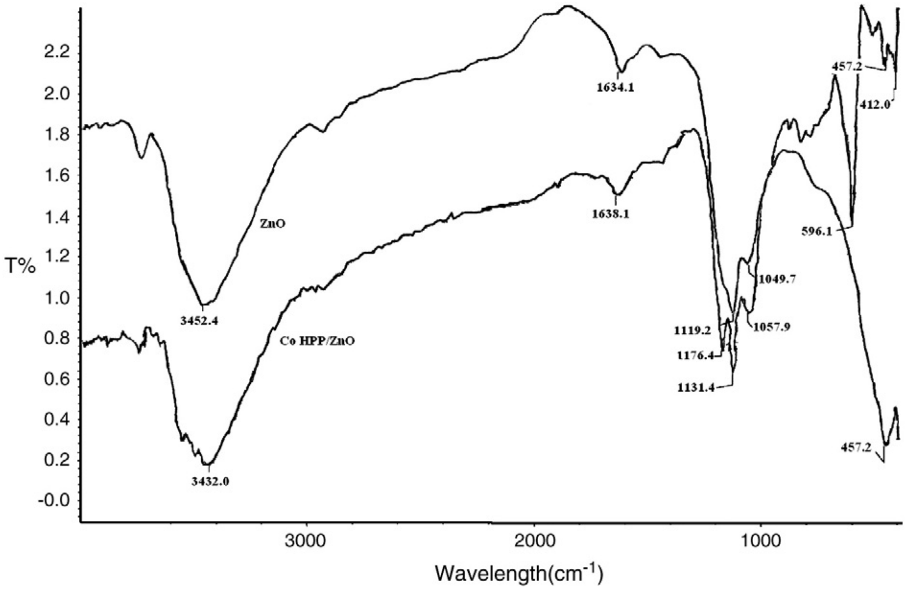

Fig. 2. FT-IR spectra of ZnO and Co THPP/ZnO with an effective frequency range of 4000–400 cm^{-1}.