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Catalytic combustion of volatile organic compounds over Co/ZSM-5 coated on stainless steel fibers

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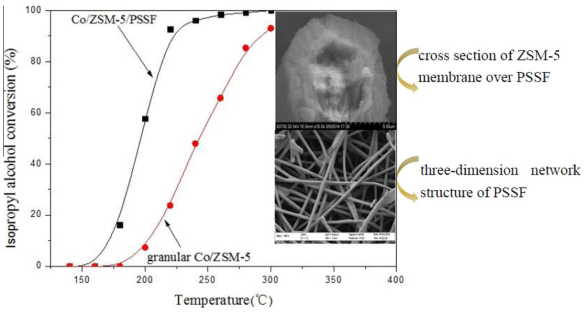
HIGHLIGHTS

- A novel gradient porous Co/ZSM-5/PSSF catalyst was prepared.
- The Co/ZSM-5/PSSF catalyst presents efficient activity for isopropanol oxidation.
- Catalytic efficiency of Co/ZSM-5/PSSF is superior to granular Co/ZSM-5.

GRAPHICAL ABSTRACT



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ABSTRACT

Co/ZSM-5/PSSF (paper-like stainless steel fibers) catalyst was prepared for the catalytic combustion of volatile organic compounds (isopropanol). The cobalt oxides modified ZSM-5/PSSF catalyst was synthesized by wet impregnation method, and the ZSM-5/PSSF was prepared via secondary growth method on the surface of PSSF supports which was made by wet lay-up papermaking method and sintering process. Characterization of all the samples was carried out by means of X-ray diffraction (XRD), scanning electron microscope (SEM), energy disperse X-ray spectrometer (EDS) mapping, X-ray photoelectron spectrum (XPS), N_2 adsorption/desorption and H_2-temperature programmed reduction (H_2-TPR). The results of EDS demonstrated that cobalt oxides had a perfect dispersion on the surface of ZSM-5/PSSF. The performance of catalytic oxidation of single VOCs (isopropanol) was conducted over a zeolite membrane reactor based on Co/ZSM/PSSF catalysts, the experimental results showed that the 0.5 M Co/ZSM-5/PSSF-500 °C catalyst exhibited the best catalytic activity for isopropanol oxidation with 90% conversion of isopropanol at 222 °C with the feed concentration of 4.5 mg/L and GHSV of 7643 h^{-1}, which was much lower than that of granular Co/ZSM-5 catalyst (293 °C). The special pore structure of ZSM-5/PSSF can offer a relatively higher contacting efficiency, lower diffusion resistance and reasonable mass/heat transfer efficiency.

1. Introduction

Volatile organic compounds (VOCs) are important group of air pollutants, which are emitted to the atmosphere mainly from industry, transports and residential/service sector [1,2]. VOCs, even in very low concentrations, are associated with various health-related problems and environmental destructions because of their toxicity, malodorous nature and relatively high vapor pressure [1,3]. Many different techniques for VOCs removal have been developed, for example, adsorption [4,5], biotechnology [6], condensation [7], membrane separation [8] and different types of oxidation (thermal oxidation and catalytic oxidation) [9]. Catalytic oxidation is one of the most attractive ways, in this very procedure,

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relatively high destructive efficiencies can be achieved at low temperatures resulting in considerable environmental and economic benefits in comparison to the traditional thermal oxidation [10,11]. Also, catalytic oxidation appears to be more efficient for the low concentration of contaminants (<1000 ppm), which cannot be thermally combusted without additional fuel [4].

Employed catalysts for catalytic combustion are mainly supported noble metals [12,13] and transition metal oxides [14–16]. As for noble metals, which present higher activity and are more active at relatively lower temperature than any other metal oxides [17], however, their high manufacturing cost, low thermal stability and tendency to poisoning limit their wide use in industry [14,18]. On the other hand, transition metal oxides offer lots of technical and commercial advantages that make them a crucial selection over noble metals [19–22]. Among the transition metal oxides, cobalt oxides such as Co_2O_3 and Co_3O_4 were reported to exhibit efficient catalytic performance for the oxidation of VOCs, and it has been widely used for the total oxidation of VOCs [11,23–25].

The support materials play a determinant role in the dispersion of the active component on the surface, thus influencing the catalytic activity. Zeolites that can stabilize and provide high surface area support for transition metals have been claimed as promising supports because of their special pore structures, acidic properties, good thermal stability and ion exchange properties [26,27]. On the basis of pore structure, microporous (NaX, ZSM-5) [1,28] and mesoporous (MCM-41, SBA-15) [22] zeolite with different channel systems are two important zeolites from the catalytic and industrial point of view [29]. Among them, metal modified ZSM-5 was intensively investigated for catalytic combustion of VOCs [26,30–32]. However, the industrial application of these granular or powder catalysts have been limited because of the relatively higher mass transfer resistance and bed pressure drop, as well as lower contacting efficiency exit in the traditional fixed bed reactor [33]. Recently, several structured supports such as aluminum foams, zeolite coated cordierite foams and zeolite membrane-coated microreactor channels which can well reduce these disadvantages have been widely applied in the preparation of catalysts that related to the combustion of VOCs. Sanz et al. reported the aluminum foams was used as structured supports for volatile organic compounds oxidation and the catalysts obtained showed outstanding results in toluene complete oxidation [34]. The catalytic combustion of toluene on Pt zeolite coated cordierite foams has been investigated and the good dispersion of Pt particles on the external surface of zeolite crystallites undoubtedly increased the catalytic activity for toluene combustion [35]. Navasces et al. investigated the combustion of volatile organic compounds at trace concentration levels in zeolite-coated microreactors and results showed that zeolite-coated microreactors are highly efficient contactors for the combustion of VOCs [36]. Previous investigations in our group indicated that ZSM-5 zeolite membranes with obvious advantages of high specific surface area, uniform pore structure as well as chemical stability would be widely used for VOCs removal, which can well lessen the defects of traditional granular or powder catalysts [37].

Isopropanol is one of the typical gaseous pollutants and presents a high level of toxicity, and it's an important solvent and reactant in several industrial processes that emitted to atmosphere in relatively large concentrations. In this research, isopropanol was selected as the model VOCs. The main project of this research were to (1) prepare and characterize a well-designed novel gradient porous catalyst containing cobalt oxides, supported on ZSM-5 membrane over paper-like stainless steel fibers (PSSF); (2) investigate the catalytic activity of a series of Co/ZSM-5/PSSF catalysts for isopropanol oxidation over a zeolite membrane reactor and (3) compare the catalytic efficiency difference between Co/ZSM-5/PSSF catalyst and granular Co/ZSM-5 catalyst.

2. Experimental

2.1. Materials

Columnar ZSM-5 with an average diameter of 2 mm was purchased from the Catalyst Plant of Nankai University (Tianjin, China). Stainless steel fibers with an average diameter of 6.5 μm were purchased from Huitong Advanced materials Company (Hunan, China). Tetrapropylammonium hydroxide (TPAOH, 25% in water) was obtained from Sigma–Aldrich. Tetraethyl orthosilicate (TEOS, >99%), isopropanol (>99.5%) and the cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Ethanol (C_2H_5OH, >99.8%) was purchased from Sinopharm Chemical reagent (Beijing, China).

2.2. Catalyst preparation

The novel gradient porous ZSM-5/PSSF (paper-like stainless steel fibers) composites were prepared by secondary growth process on the surface of PSSF (synthesized by wet lay-up papermaking and sintering process) according to the previous research in our group [37]. The metal oxides modified ZSM-5/PSSF catalysts were prepared by impregnation with 30 mL aqueous solution containing knowing amounts of $Co(NO_3)_2.6H_2O$ of 0.1, 0.25 and 0.5 M, and the excess of water was removed in an oven at 100 °C until dryness, the as-synthesized samples was dried at 100 °C for 12 h and subsequently calcined in air for 4 h, the calcination temperature was adjusted at 350, 500 and 650 °C.

2.3. Catalyst characterization

X-ray diffraction patterns (XRD) of samples were performed on a D8 Advance (Bruker Co.) diffractometer using Cu Kα radiation (40 kV, 40 mA). The diffractometer were recorded in the 2θ range of 5–80° with a 2θ step size of 1° and a step time of 10 s. The morphologies of the samples were observed by scanning electron microscopy (SEM, LEO-1530VP). Before analysis, all of the samples were coated with an ultrathin film of gold to make them conductive. The nitrogen adsorption and desorption isotherms were measured on a 3H-2000PS1 instrument in static measurement mode. All of the samples were outgassed at 150 °C for 2 h before measurements. The specific area was calculated using Brunauer–Emmett–Teller (BET) mode, the total pore volume was calculated by the analysis of N_2 adsorption–desorption isotherms, the micropore volume ($V_{\text{micro-pore}}$) and the mesopore volume ($V_{\text{micro-pore}}$) were calculated by HK (Horvath–Kawazoe) method and BJH (Barrett–Joyner–Halenda) method, respectively. The X-ray photoelectron spectroscopy (XPS) measurements were obtained by using a Kratos Axis Ultra (DLD) spectrometer with an Al Kα (1486.6 eV) radiation source operated at 15 kV and 10 mA. The binding energy (BE) of the C1s peak at 284.6 eV was taken as a reference. H_2-Temperature programmed reduction (TPR) tests were conducted on Quantachrom Automated Chemisorption Analyzer by heating the catalyst in H_2 (10 vol%)/Ar flow (30 ml min^{-1}) at a heating rate of 10 °C min^{-1} from room temperature to 700 °C. The hydrogen consumption was detected by thermo-conductivity detector (TCD). Before analysis, the samples were loaded into the reactor and purged with helium (30 ml min^{-1}) at 300 °C for 1 h to eliminate contaminants, and then cooled down to room temperature.

2.4. Catalytic test

The catalytic test of Co/ZSM-5/PSSF catalysts for isopropanol oxidation was carried out in a fixed bed reactor with a stainless steel tube (10 mm i.d., 450 mm length) at atmosphere pressure.