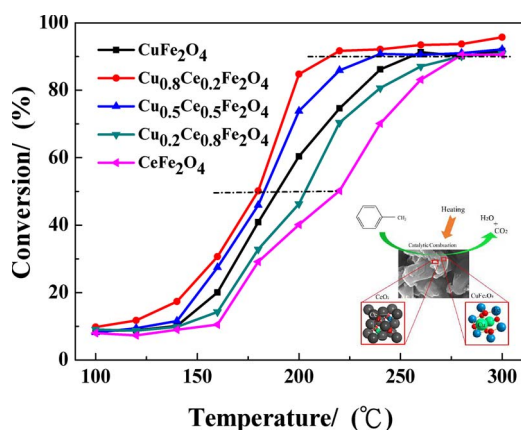


Effects of Ce in the catalytic combustion of toluene on $\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$ Yongqiang Wang^{a,b,*}, Rui Xue^a, Chaocheng Zhao^{a,b}, Fang Liu^{a,b}, Chunshuang Liu^a, Fenglei Han^a^a College of Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, PR China^b State Key Laboratory of Petroleum Pollution Control, China University of Petroleum (East China), Qingdao 266580, PR China

GRAPHICAL ABSTRACT

Catalytic combustion performance of toluene over $\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$.Catalytic combustion performance of toluene over $\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$

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ABSTRACT

$\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.5, 0.8, 1$) catalysts were synthesized by a sol-gel auto-combustion method, and the catalysts were characterized by differential thermal analysis (DTA), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM), H_2 -temperature-programmed reduction (H_2 -TPR), and X-ray photoelectron spectroscopy (XPS). The activity of $\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$ was evaluated in the catalytic combustion of toluene in a fixed-bed reactor. The results indicated that the $\text{Cu}_{0.8}\text{Ce}_{0.2}\text{Fe}_2\text{O}_4$ expressed the highest catalytic combustion activity of toluene, the ignition temperature (T50) and the complete conversion temperature (T90) were 180 °C and 215 °C, respectively. The Ce doping of CuFe_2O_4 could increase the oxygen storage capacity and improve the catalytic combustion activity of toluene. The CuFe_2O_4 spinel crystal structure gradually disappeared with the increase in Ce doping; at the same time, the catalytic combustion activity of the samples was obviously affected.

1. Introduction

Volatile organic compounds (VOCs) have been recognized as major

contributors to air pollution because of their toxicity, carcinogenicity, mutagenicity and teratogenicity [1]. Various technologies were applied to eliminate the VOCs, such as adsorption, bio-degradation, membrane

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separation, and so on. In contrast to other technologies, the catalytic combustion process is the better one because of its higher efficiency, energy conservation and no secondary pollution [2]. The preparation of highly active catalysts is a key research field of catalytic combustion; among the kinds of catalysts, the spinel catalyst (AB_2O_4) is widely used in the catalytic combustion of VOCs because of their thermal stability and oxygen mobility. Tasca reported that CuFe_2O_4 possessed the inverted spinel and a high specific surface area, which could enhance the catalytic combustion activity of the VOCs in CuFe_2O_4 [3]. Zawadzki prepared ZnAl_2O_4 substituted with Co^{2+} and Fe^{3+} . It was found that the spinel structure was helpful for the catalytic combustion of propane, and the substitution of the larger-ionic-radius Fe^{3+} and Co^{2+} could increase the unit cell parameter and volume, which could cause the catalysts to be very resistant to hydrogen reduction. Liu found that Mn substitution could increase the lattice oxygen content, facilitate the reduction of ferrite, and enhance the oxidative ability of Fe and Mn cations on the catalyst surface. The presence of Mn cations in spinel ferrite greatly improves its catalytic activity in formaldehyde oxidation [5]. Zhou discussed the catalytic combustion activity of a spinel Cu-Mn catalyst. It was found that the strong interaction of Mn and Co species and Co-Mn composite compounds could weaken the Mn–O chemical bonds, which could enhance the catalytic combustion activity of the spinel [4]. Among kinds of the doping elements, the Ce oxide was proved to have a high oxygen storage capacity, which could improve the catalytic combustion activity of active species [5]. Zhu combined the Fe_2O_3 and CeO_2 , and found that Fe_2O_3 particles were well dispersed on the ceria surface, and a small amount of Fe ions was incorporated into CeO_2 to form a Ce-Fe-O solid solution. The strong Ce-Fe interaction in the system could significantly improve the redox activity of the catalyst [6]. Zeng [7] synthesized the CeO_2/CuO catalysts. The particle and rod-like CeO_2 were found in the catalysts, and the rod-like CeO_2 exposed more (111) planes of CeO_2 with oxygen storage and transportation. Fei et al. [8–10] have designed and prepared some samples with hierarchical hollow nanostructures in order to improve the catalytic activity of MnO_2 , TiO_2 and ferric hydroxide, and think the hierarchical porous structures are very beneficial for some catalysis reaction.

In this paper, $\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.5, 0.8, 1$) were prepared by the sol-gel auto-combustion method, and the catalytic activity of $\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.5, 0.8, 1$) was tested by the degradation of toluene. To analyze the effect of Ce doping of the spinel catalyst CuFe_2O_4 , the samples were characterized by DTA, FT-IR, XRD, N_2 adsorption-desorption, SEM, H_2 -TPR and XPS.

2. Experimental

2.1. Catalyst preparation

The catalysts were synthesized via the sol-gel auto-combustion method. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (AR), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR) were dissolved in distilled water to obtain a mixed metal nitrate solution (the molar ratio of Fe:(Cu + Ce) was 2:1). Citric acid was dissolved in distilled water with a mole ratio of citric acid and metal nitrate of 1:1. The citric acid solution was added into the metal nitrate solution slowly, and then the mixed solution was obtained. The solution was stirred at 200 r min^{-1} and heated at $70 \pm 5^\circ\text{C}$, at the same time the pH value was controlled at 7 ± 0.5 by adding ammonia. The solution formed a colloid after it was stirred for 5 h and was aged at room temperature for 2 h and dried for 12 h at 130°C to obtain the dry gel. The dry gel was ground into powder, and the powder was burned with an auto-combustion method until all the gel was completely combusted to form the loose tree-like powder and was calcined at 500°C for 2 h to remove the residual organic matter and form the spinel crystal catalysts. The 40–60 mesh granular catalysts were produced by powder catalyst after tableting and sieving.

2.2. Catalysts evaluation

The toluene catalytic combustion activity was investigated in a continuous flow fixed-bed stainless steel tube reactor (i.d. = 30 mm, length = 550 mm) at temperature range $100\text{--}300^\circ\text{C}$, the catalyst bed was heated at a ramp rate of $10^\circ\text{C min}^{-1}$. The catalyst (5 ml, 40–60 mesh) was mixed with quartz sand (10 ml, 40–60 mesh) and was fixed in the middle of the reactor. The concentration of the toluene was 300 mg m^{-3} , the velocity was 500 ml min^{-1} , and the gas hourly space velocity (GHSV) was 6000 h^{-1} , the pressure inside the reactor was 0.8 MPa. The inlet and outlet concentration of toluene was analyzed by SP-3420 (Beijing Beifen-Ruili Analytical Instrument Co., Ltd.) equipped with a flame ionization detector (FID) and capillary column. The temperature of the column, the inlet and detector were 200°C , 150°C and 120°C , respectively.

2.3. Catalysts characterization

Differential thermal analysis of the dried gel was recorded from 20°C to 700°C with a heating rate of 1°C min^{-1} under air atmosphere in HCT-2 Differential Scanning Calorimeter (Beijing Henven Scientific Instrument Factory, China). X-ray diffraction patterns (XRD) were characterized by an X'Pert Pro MPD power diffractometer (PANalytical Co.) with a Ni filter and Cu-K α ray at 40 kV and 50 mA. The samples were scanned of 2θ from 5° to 75° with the scan rate of $4^\circ/\text{min}$. The N_2 adsorption-desorption isotherms were collected at -196°C on an ASAP-2020M Micropore Physisorption Analyzer (Micromeritics Instrument Corporation, USA). The samples were degassed in vacuum at 300°C for 5 h, before the measurement of nitrogen. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) gravimetric method, and the pore size distribution and average pore diameter were obtained on the desorption branch of the N_2 isotherm by the Barrett-Joyner-Halenda (BJH) method. Fourier transform infrared (FT-IR) were carried out in the range of $4000\text{--}400 \text{ cm}^{-1}$ on a NEXUS FT-IR spectrometer (Thermo Nicolet Corporation, USA) by the KBr pellet method. Scanning electron microscopy (SEM) was taken on a Merlin Compact instrument (Carl Zeiss Jena, Germany) with an InLens detector operating at 15 kV. The H_2 -temperature programmed reduction (H_2 -TPR) was performed in a TP5079 multi-purpose chemical adsorption instrument (Tianjin Xianquan, China) at 30 mA and 60°C with a thermal conductivity detector under flowing (20 ml/min) 10% H_2/Air . First, 100 mg of the catalyst samples were heated at 300°C for 0.5 h to remove the impurities and were determined at $100\text{--}800^\circ\text{C}$ with a heating rate of $10^\circ\text{C}/\text{min}$. X-ray photoelectron spectroscopy (XPS) was measured on an Escalab 250Xi spectrometer (Thermo Fisher Scientific, USA) with Al K α X-rays and $500 \mu\text{m}$ beam spot; the binding energy (BE) was calibrated with from the C1s (284.8 eV).

3. Results and discussion

3.1. Catalytic combustion activity of toluene over $\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$

The catalytic combustion activity of toluene over $\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$ at 6000 h^{-1} (GHSV) from 100°C to 300°C is shown in Fig. 1, and the T50 and T90 (the temperature of 50% and 90% toluene conversion, respectively) is listed in Table 1. It was found that the doping content of Ce could greatly affect the catalytic combustion activity of $\text{Cu}_x\text{Ce}_{1-x}\text{Fe}_2\text{O}_4$, and the catalytic activity was in the order of $\text{Cu}_{0.8}\text{Ce}_{0.2}\text{Fe}_2\text{O}_4 > \text{Cu}_{0.5}\text{Ce}_{0.5}\text{Fe}_2\text{O}_4 > \text{CuFe}_2\text{O}_4 > \text{Cu}_{0.2}\text{Ce}_{0.8}\text{Fe}_2\text{O}_4 > \text{CeFe}_2\text{O}_4$. As shown in Fig. 1, the $\text{Cu}_{0.8}\text{Ce}_{0.2}\text{Fe}_2\text{O}_4$ catalyst exhibited the best activity for toluene, and T50 and T90 were 9°C and 40°C lower than CuFe_2O_4 , respectively. The Cu and Fe atoms were doped into the CeO_2 crystal to form the Cu-Fe-Ce solid solution according to the analysis of XRD, which could improve the oxygen storage capacity (OSC) when suitably doping the Ce [11]. As shown in Fig. 4, the CuFe_2O_4 spinel crystal gradually disappeared when the ratio of Cu:Ce was

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