Catalytic combustion of volatile organic compounds over Rh-Cu co-catalyst supported by H-ZSM-5 zeolite

Abstract

Introduction

1. volatile organic compounds (VOCs) are one of major air contaminants, which is defined by WHO, as organic compounds generally having boiling points within the range of 50 ~ 260 ℃. The VOCs covers many varieties of substances, from simple alkanes to polycyclic aromatic hydrocarbons, contributing both indirectly as ozone / smog precursors and directly as substances hazardous to the environment or human health. 【】Although, the VOCs are present in very low concentration, they have very serious health-related issues and bad environmental impacts due to their high vapor pressure, odor and toxicity. Owing to rapid urbanization and industrialization, the emission of VOCs into environment has increased rapidly, which can be from a wide range of outdoor and indoor sources. Outdoor sources, which include but are not limited to chemical industries, paper production, food processing, paint drying, transportation, petroleum refineries, are major compared with indoor sources of the VOCs emission from household products, office supplies, printers, insulating materials, heat-exchanger systems and pressed woods, etc. Hence, there is more increasingly strict legislation for stringent emission of industrial VOCs, causing the technologies to control VOCs emission as a very important topic of research. Apparently, the best way to reduce the emission of VOCs is to replace VOCs or to limit their use in industrial processes. If VOCs substitution is not probable, it is necessary for VOCs removal to use methods based on recovery and destruction, after improving reaction conversion and yield by optimizing original process conditions. The techniques based on recovery include absorption, adsorption, membrane separation and condensation, while the destruction methods can be thermal, catalytic, plasma, biological oxidation. Among these techniques, catalytic oxidation is widely used in industrial area, regarded as the most efficient and economical way with low operating temperature and generation of less secondary pollution. According to previous report, catalytic oxidation is the most favorable for effluent streams with low concentration of VOCs, so it is highly valid to control end-of-pipe VOCs pollution. Due to the dependence of the catalytic combustion on catalysts, it is pivotal to search for suitable catalytic material with high activity, high tolerability and universality.
2. Numerous catalysts have been developed for VOCs oxidation, which are mainly based on noble metal, transition metal oxides and zeolite. The activity of zeolites in removal of some VOCs is attributed to their acidic properties. Furthermore, they are often chosen as supports because of their superior and tunable surface properties, hydrophobicity and metal loadability, allowing the high dispersion of active phases and generating the interaction between the active phases and the support. It is often supposed that noble metal catalysts are very efficient, due to their remarkable activity at low temperatures and adequate stability. However, low resistance to halogens and high expense of noble metal somewhat restrict their widely practical application. In contrast, transition metal oxides, especially Cu, Ce, Mn, attach more and more attention for its low costs, better tolerability to poison, and high thermal stability. Recently, mixed oxides especially bimetallic catalysts have been widely reported that they show higher activity, selectivity, and stability than monometallic materials. This is mainly attributed to the synergistic interactions between the different metal species toward enhancing catalyst reducibility.
3. In comparison to the other precious metals especially palladium and platinum, Rhodium catalysts are far less explored in catalytic oxidation reactions.【】 Rhodium catalysts still have great value and research significance in catalytic combustion of VOCs due to the metallic electronic structure of rhodium which contributes to lattice defects and active metal species generation of rhodium catalysts, although the catalytic oxidation activities of them are not outstanding among metal oxides catalysts.
4. Copper oxide is one of the most commonly used metal oxide-based catalysts for oxidation reactions. 【】
5. The ZSM-5 zeolite is formed from the pentasil unit, which are interconnected by an oxygen bridge resulting in 10-membered ring. ZSM-5 zeolite loaded with metal oxides have become very research-worthy catalysts for VOCs removal. ZSM-5 can be used as support for metal oxides that improve their catalytic efficiency and the definite structure of ZSM-5 could limit the over growth or sintering of metal particles to keep them active. On the other hand, as demonstrated elsewhere, the VOCs adsorption capacity of ZSM-5 zeolites can be decreased or increased by metal loading due to the reduction of specific surface area and the strong interaction between metal ions and VOC molecules respectively. 【】
6. Accordingly, it is of great interests to attempt to prepare rhodium and copper bimetallic co-catalysts supported by ZSM-5 for VOCs combustion. Consequently, a series of Rh-M/HZSM-5 samples are prepared by impregnation and evaluated in the catalytic oxidation of toluene in the present study. It was found that the Rh-Cu/HZSM-5 sample was the most active catalyst. The influence of CuO content and Si / Al ratio of HZSM-5 was also studied. Then,

Experimental

1. Chemicals and materials
2. Catalyst preparation

The Rh-M/HZSM-5(M=Cu, Mn, Ce, Co, Ag) samples are synthesized using incipient wetness co-impregnation method technique. The theoretical loading of Rh and M were kept equal to all catalysts, which were 1 wt.% and 3 wt.%, respectively. In a typical preparation of 1Rh-3Cu/HZSM-5, according to the water adsorption of HZSM-5 (Si / Al =50), \* and \* were dissolved into a certain volume of aqueous solution. HZSM-5 (Si / Al =50) was added in the aqueous solution and then the mixture was stirred at room temperature for 4 hours. Subsequently, after dried at 120 ℃ for 12 hours, the solid was calcined in a muffle oven with a rate of increase of 5 ℃ min-1 from 25 to 400 ℃ and kept at this temperature for 4 hours, giving the target sample denoted as 1Rh-3Cu/HZSM-5 (Si / Al =50). Meanwhile, 1Rh/HZSM-5 (Si / Al =50) and 3Cu/HZSM-5 (Si / Al =50) were prepared for comparison, by using impregnating solution containing only one metal nitrate, \* or \* respectively. 1Rh-yCu/HZSM-5 (Si / Al =50, y=1, 3, 5, 10) and 1Rh-3Cu/HZSM-5 (Si / Al =25, 38, 50, 60, 70) were synthesized by the same method with adjusting the amount of ….. and the Si / Al ratio of HZSM-5 support.

1. Catalyst characterization

The Rh and Cu content of catalyst samples were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES….). X-ray diffraction (XRD) patterns of the samples were recorded on Rigaku D/max 2500 (Rigaku Corporation, Japan) using a Cu Kα X-ray source (40 kV, 100 mA) in the range of 10-90°. Transmission electron microscopy (TEM) images were recorded via a Jeol JEM-2100F microscope operating at an electron beam voltage of 200 kV. Powder samples were supported on a …grid for TEM analysis. ………

1. Catalytic evaluation

The catalytic combustion of VOCs experiments were implemented on the fixed bed reactor (i.d. = …, length = ….) to evaluate the catalytic performance from 150 ℃ to 500 ℃ with 2-2.5 cm catalytic bed height and 600 mg of catalysts (60-80 mesh). The reaction temperature was improved step-by-step and the reaction was kept about 60 min at each temperature point to ensure reaching steady reaction equilibrium and the total reaction pressure in the reactor was approximate 0.12 MPa. Organic compound feed was injected into a vaporization chamber by a metering pump, mixed with air from gas cylinder and its theoretical concentration was 500 ppm. the VOC concentration in total flow of reactant mixture was calibrated by gas chromatography (GC…..) through a bypass. The outlet gas from the reactor was analyzed by the on-line gas chromatography (GC) equipped with an FFAP capillary column and an FID detector, before exhausted through buffer. The conversion of …(X) was calculated by inlet (Cin) and outlet (Cout) concentration in the equation below

×100%

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Result and Discussion

1. catalyst oxidation of VOCs

The catalytic oxidation of toluene over all catalysts was carried out under the condition of 500 ppm toluene at a WHSV of ….. within 150 - 500 ℃. As shown in Fig 1, the T50 and T90 of 1Rh-3Cu/HZSM-5 were 253 ℃ and 262 ℃ respectively, which are obviously lower than monometallic catalyst 1Rh/HZSM-5 (292 ℃ and 306 ℃). In addition, comparing to 1Rh/HZSM-5, 1Rh-3Mn/HZSM-5 and 1Rh-3Ce/HZSM-5 did not show a more clearly increase in catalytic activity and the other catalyst systems showed a negative effect for toluene oxidation. Notably, 1Rh-3Cu/HZSM-5 had the lowest complete oxidation temperature of 273 ℃, proving that Rh-Cu catalyst system is more efficient and

