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Efficient oxidative degradation of 2-chlorophenol and 4-chlorophenol over supported CuO-based catalysts

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Abstract

A series of metal oxide catalysts for catalytic oxidative degradation of 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP) were prepared, and the supported CuO catalysts were studied particularly. The supported CuO catalysts were characterized by XRD and NH_3-TPD techniques, in which CuO/γ-Al_2O_3 exhibited high degradation activity. The addition of Na_2O or K_2O into CuO/γ-Al_2O_3 improved the oxidative degradation of CPs remarkably, in which Na_2O was more efficient than K_2O. Over CuO/γ-Al_2O_3-Na_2O, CPs were completely converted and the liberation of the inorganic chloride from 2-CP or 4-CP reached 97% or 100% respectively at 30 °C for 2 h. The supported CuO catalysts with good dispersion of CuO particles and less acid sites were favorable for the efficient oxidative degradation of CPs. In addition, the initial pH of the reaction solution was found to be an important factor which influenced the catalytic oxidative degradation of CPs and the initial pH of 11.2 and 9.8 was preferred for the oxidative degradation of 2-CP and 4-CP respectively over CuO/γ-Al_2O_3 catalyst.

Key words

CuO/γ-Al_2O_3; Na_2O; K_2O; chlorophenol; oxidative degradation

1. Introduction

For several years, environmental problems have received increasing social and political attention. Chlorophenols (CPs), widely used as preservative agents for wood, paints and vegetable fibers, disinfectants and intermediates [1−6], are now recognized as a particular group of top toxic pollutants [7,8]. Most CPs are hardly biodegradable and very difficult to be removed from the environment [9]; therefore, to protect environment, the development of highly efficient approach for the degradation of CPs is an important research target.

To date, various treatment techniques have been used in the removal of CPs. Among them, the conventional biodegradation process of CPs is relatively inexpensive [10], however, it is very sensitive to shock loads and requires long hydraulic retention time [11,12]. Physico-chemical technologies, such as activated carbon adsorption, just transfer CPs from one phase to another, leaving the problem only partially solved [13,14]. Oxidation method has been given considerable attention in recent years for the degradation of CPs. Wet air oxidation (WAO), however, is performed under high pressure (5−17.5 MP) and high temperature (200−325 °C) under which serious corrosion problems caused by HCl produced during the decomposition process may arise [15]. Catalytic oxidation, one of the most promising technologies, was frequently reported in the literatures [16−20]. Hetrick et al. studied the catalytic oxidation of 2-CP over V_2O_5/TiO_2 catalyst and the conversion of 2-CP reached 100% at the high temperature of 275 °C [16]. Li et al. studied the catalytic oxidative degradation of 4-CP and the removal of 4-CP reached 80% after 400 min of the reaction at 25 °C over copper complex of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetrae-ne copper (II) [19]. Kim et al. investigated the degradation of 4-CP over three copper catalysts of CuO, CuO/γ-Al_2O_3 and CuO/γ-Al_2O_3-ZnO, and found that the removal of 4-CP reached 20%, 65% and 50%, respectively at 28 °C for 2 h [20].

In this work, a series of metal oxide catalysts were tested for the oxidative degradation of 2-CP and 4-CP and the

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catalytic activities of supported CuO catalysts were studied particularly. Alkali metal oxide such as Na_2O or K_2O was introduced into CuO/γ-Al_2O_3 catalyst to promote the oxidative degradation of the CPs. XRD and NH_3-TPD techniques were used to reveal the relationship between the structure of supported CuO catalysts and the catalytic degradation activity. Active component loading and the initial pH of 2-CP or 4-CP solution were also investigated.

2. Experimental

2.1. Preparation of catalysts

Metal oxide catalysts were obtained by calcining metal nitrates at 500 °C for 4 h. Supported CuO catalysts were prepared by incipient wetness impregnation using SiO_2, γ-Al_2O_3 or SiO_2-Al_2O_3 as support. The support was impregnated in appropriate amount of copper nitrate aqueous solution for 15 h at room temperature, dried at 120 °C for 4 h, and then calcined at 500 °C for 4 h in air. The CuO/γ-Al_2O_3 catalyst doped with Na_2O or K_2O was prepared by sequential impregnation. Na_2O or K_2O was first loaded on the surface of γ-Al_2O_3, followed by CuO loading and the process was the same as the preparation of the CuO/γ-Al_2O_3 catalyst.

2.2. Evaluation of catalytic activity

The typical reaction mixture, containing 50 mL of 2-CP or 4-CP aqueous solution (100 ppm), a certain amount of catalyst and 1 mL of 30% hydrogen peroxide, were kept in a closed glass vessel at temperature of 30 °C using a thermostated bath. Reaction sample was withdrawn at specific time interval and the catalyst was immediately separated from the aqueous phase by centrifugation. Analysis of chloride ion in the aqueous solutions was carried out with chloride ion-selective electrode.

The conversion of 2-CP or 4-CP was determined by HPLC (Shimadzu) equipped with an UV detector at 275 nm and a 150 mm×4.6 mm C18 reverse phase column. The mobile phase was a mixture of 50 vol% methanol and 50 vol% water (both with 1% acetic acid) with a flow rate of 1.0 mL/min, and the injection volume was 20 μL.

The by-products were analyzed on a gas chromatograph with a mass spectrometer (Agilent GCMS 6890N-5975B) equipped with a HP-5 capillary column.

2.3. Characterization of catalyst

The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max 2400 diffractometer with Cu K_α radiation source at a rate of 0.5 °/min in the 2θ range of 30^o-80^o. The voltage and current were 40 kV and 40 mA, respectively.

The temperature-programmed desorption of ammonia (NH_3-TPD) was carried out in a quartz reactor with inside diameter of 6 mm and length of 350 mm. Before adsorption, 150 mg of the sample was pretreated at 500 °C for 1 h in a flow (35 mL/min) of ultra pure helium gas to remove water from the catalyst. Then, the sample was saturated with ammonia gas at 100 °C for 1 h and subsequently flushed with He (35 mL/min) at 100 °C for 1 h to remove the physisorbed ammonia, in which the heating rate was 10 °C/min and the temperature range was from 100 °C to 700 °C.

3. Results and discussion

3.1. Oxidative degradation of CPs over metal oxide catalysts

Several metal oxides were used as catalysts for the oxidative degradation of 2-CP and 4-CP. Their conversion and the liberation of the inorganic chloride from 2-CP or 4-CP are shown in Table 1. It can be seen that about 35% 2-CP or 33% 4-CP was converted for 6 h and only 1% inorganic chloride was detected without the catalyst. When metal oxides, such as Fe_2O_3, Co_3O_4, NiO, V_2O_5, MoO_3, WO_3 or MnO_2, were employed as a catalyst, both the conversion of CPs and the liberation of the inorganic chloride increased. Among all the tested catalysts, CuO exhibited the highest activity for the oxidative degradation of CPs, over which the conversion of the CPs reached 100% and the liberation of the inorganic chloride from 2-CP or 4-CP reached 46% or 52%, respectively, for 6 h.

Table 1. The oxidative degradation of CPs over different metal oxide catalysts

Catalyst	Conversion (%)		Liberation of the inorganic chloride (%)	
	2-CP	4-CP	2-CP	4-CP
No catalyst	35	33	1	1
Fe_2O_3	54	59	23	19
Co_3O_4	59	62	11	22
NiO	55	54	15	14
V_2O_5	39	44	13	17
MoO_3	38	42	7	7
WO_3	44	51	10	10
MnO_2	38	46	8	5
CuO	100	100	46	52

Reaction conditions: 30 °C, 0.048 g catalyst, reaction time of 6 h

3.2. Oxidative degradation of CPs over supported CuO catalysts

Table 2 shows the results of oxidative degradation of 2-CP and 4-CP over the catalysts of SiO_2, γ-Al_2O_3 or SiO_2-Al_2O_3 and the supported CuO. It can be seen that over the supported CuO catalysts, the conversion and the liberation of the inorganic chloride from 2-CP or 4-CP were much higher than those over the corresponding supports. Among them, CuO/γ-Al_2O_3 exhibited the highest activity. Over CuO/γ-Al_2O_3 catalyst, CPs were completely converted and the liberation of the inorganic chloride from 2-CP or 4-CP reached 70% or 76% respectively for 2 h.