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An efficient Cu-K-La/γ-Al_2O_3 catalyst for catalytic oxidation of hydrogen chloride to chlorine

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ABSTRACT

An efficient Cu-K-La/γ-Al_2O_3 catalyst, prepared by the incipient wetness impregnation method, was developed for the catalytic oxidation of HCl to chlorine, in which effects of catalyst composition, calcination temperature, reaction temperature and GHSV of the feed gas and the catalyst stability were investigated. Cu-K-La/γ-Al_2O_3 catalyst shows good catalytic performance and stability with the conversion of HCl of about 78% for reaction for over 9600 h under the reaction conditions of 30 g catalyst, 0.1 MPa, 340 °C, GHSV of 450 L/(kgcat h), HCl/O_2 = 2:1. Thermogravimetry results indicate that the synergistic promoters of KCl and $LaCl_3$ can significantly reduce the reaction temperature for oxidation of $CuCl_2$ to produce chlorine, which is a key step in the catalytic oxidation of HCl. XRD results show that there were only broad characteristic diffraction peaks of γ-Al_2O_3 support and copper species, potassium species and lanthanum species were highly dispersed on the surface of γ-Al_2O_3 support over Cu-K-La/γ-Al_2O_3 catalyst.

1. Introduction

Toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), key raw materials for manufacture of polyurethanes, are usually produced by phosgenation of the corresponding diamine precursors, in which chlorine reacts with carbon monoxide to produce phosgene. In manufacture of TDI or MDI, the byproduct of HCl is produced four times the molar amount of TDI or MDI. The demands for TDI and MDI are increasing sharply, which results in the inevitable production of much excessive HCl more than its market demand, serious disposal problem of toxic waste and thus cannot meet the increasingly stringent environmental regulations. Therefore, more strategies have been pursued to develop an efficient method for recycling chlorine from HCl to design a closed recycle process in the chlorine-related industries [1–4].

The processes recycling chlorine from HCl include three processes as follows [5,6]: (1) Electrolysis of HCl to produce Cl_2 and H_2 with the disadvantage of the electrodes generating great amounts of CO_2 equivalent due to their large electricity consumption. (2) Cyclic oxidation of HCl by sulfuric acid as a circulating cyclic medium under a nitrogen oxide catalyst with very high capital cost due to the complexity of the process. (3) Catalytic oxidation of HCl to chlorine by air or O_2 (so-called Deacon process) over Cu-Dy-K/SiO_2 catalyst (Shell-Chlor process) [7], Cr_2O_3/SiO_2 (MT-Chlor process) [8], RuO_2/rutile-TiO_2 catalyst (Sumitomo process) [5] and RuO_2/SnO_2-Al_2O_3 catalyst (Bayer process) [9,10]. Deacon process has attracted increasing attention because of its relative ease of application, lower energy consumption and thermal requirements. Moreover, the catalytic oxidation of HCl is mildly exothermic reaction and thus lower reaction temperature is favorable for increasing the equilibrium conversion. Many efforts have been made for developing more efficient catalysts for the catalytic oxidation of HCl. Supported CeO_2 catalyst showed the conversion of HCl of 70–75% for over 700 h under the reaction conditions of the molar ratio of O_2 to HCl of 4.15, $T_{inlet} = 633$ K and $P = 1$ bar [11,12]. $CuAlO_2$ catalyst showed the conversion of HCl of about 25% for over 1200 h under the reaction conditions of the molar ratio of O_2 to HCl of 4, $W/F_{0(HCl)} = 8.96\ \mathrm{g\ h\ mol^{-1}}$, $T = 653$ K and $P = 1$ bar [13,14]. RuO_2/SnO_2-Al_2O_3 catalyst showed the conversion of HCl of about 40% for 7000 h under the reaction conditions of the molar ratio of O_2 to HCl of 0.5, $W/F_{0(HCl)} = 36.4\ \mathrm{g\ h\ mol^{-1}}$, $T = 553$–653 K and $P = 0.1$ MPa [9,10]. RuO_2/rutile-TiO_2 catalyst showed the conversion of HCl of 85–90% for 15,000 h [5].

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Ruthenium-based catalysts are efficient commercialized catalysts for Deacon process; however, the high and dramatically fluctuating market price of ruthenium will limit the large-scale industrialization in the future, so it is necessary to develop other non-noble metal catalysts with low cost to replace the ruthenium-based catalysts [2,15,16]. The copper-based catalyst, invented for the first time by Deacon [17], was used for the catalytic oxidation of HCl to chlorine with the reaction temperature range of 430–475 °C. Nevertheless, copper chloride starts to evaporate at an appreciable rate above 400 °C, which results in the rapid deactivation of the copper-based catalyst. Lanthanum is often used to modify Cu/Al_2O_3 catalysts [18–20], in which La has particular functions in minimizing the formation of copper-aluminate and improving the thermal stability of alumina support, increasing the dispersion degree of Cu species and inhibiting the sintering of Cu species. In this work, Cu-K-La/γ-Al_2O_3 catalyst was developed for the catalytic oxidation of hydrogen chloride to chlorine, in which effects of catalyst composition, calcination temperature, reaction temperature and GHSV of the feed gas, and the catalyst stability for over 9600 h were investigated.

2. Experimental

2.1. Preparation of Cu-K-La/γ-Al_2O_3 catalyst

Cu-K-La/γ-Al_2O_3 catalyst was prepared by the incipient wetness impregnation method in our previous work [21], in which the weight ratio of $CuCl_2$, KCl and $LaCl_3$ was 3:1:2, and the total loading amount of the chloride precursors were 15, 20, 25, 30 and 35 wt%, respectively. The aqueous solution containing the above chloride precursors was added dropwise into γ-Al_2O_3 spherical support with 2.0 mm diameter, and then the sample was dried at 120 °C for 12 h and calcined at 400 °C in air for 4 h.

2.2. Characterization of Cu-K-La/γ-Al_2O_3 catalyst

Thermogravimetry (TG) was carried out on a Perkin Elmer Pyris Diamond TG-DTA analyzers, in which the sample was heated from 40 to 800 °C at the rate of 10 °C min^{-1} in the atmosphere of air of 100 mL min^{-1}.

TGA-MS profiles of the as-prepared and non-calcined $CuCl_2$-KCl-$LaCl_3$/γ-Al_2O_3 sample were carried out on a Perkin Elmer Pyris 1 thermogravimetric analyzer and Hiden HPR 20 mass spectrometer, in which the sample was heated from 40 to 850 °C at the rate of 10 °C min^{-1} in the atmosphere of air of 30 mL min^{-1}.

The powder XRD patterns were recorded on a Bruker AXS D8 Focus diffractometer operated at 40 kV, 40 mA (Cu Kα radiation, $\lambda = 0.15406$ nm), and the diffraction patterns were taken in the range of $10° < 2\theta < 80°$ at the scanning rate of 6° min^{-1}.

2.3. Catalytic oxidation of HCl

The catalytic oxidation of HCl over Cu-K-La/γ-Al_2O_3 catalyst was investigated in the quartz fixed-bed reactor under the reaction conditions of 30 g catalyst, 0.1 MPa, GHSV of 450 L/(kgcat h), $HCl/O_2 = 2{:}1$ (molar ratio). The flow rate of HCl and O_2 was 150 and 75 mL min^{-1}, respectively, which were introduced into the reactor by the mass flow controllers. The product of chlorine was analyzed by iodometry method and the excess hydrogen chloride was quantified by the standard sodium hydroxide solution. There was no byproduct in the catalytic oxidation of HCl, therefore the selectivity of chlorine was 100%, and the value of the conversion of HCl was equal to that of the yield of chlorine.

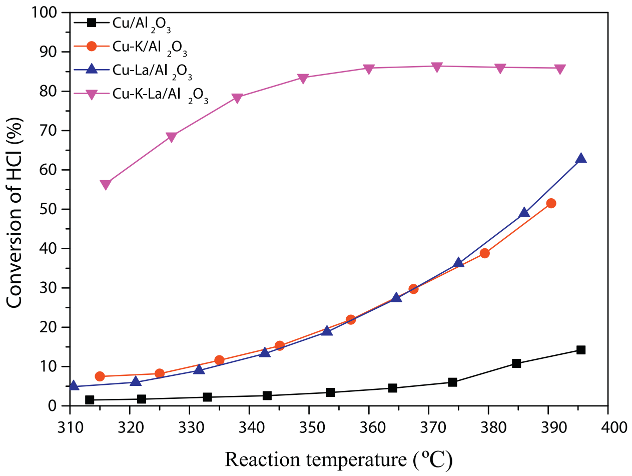

Fig. 1. Catalytic performance of the copper-based catalysts with different catalyst compositions for HCl oxidation.

3. Results and discussion

3.1. Catalytic oxidation of HCl

3.1.1. Effect of catalyst composition

Fig. 1 shows the catalytic performance of the copper-based catalysts with different catalyst compositions for HCl oxidation. As shown in Fig. 1, Cu/γ-Al_2O_3 catalyst had the worst catalytic activity with the maximum conversion of HCl of 14.2% at 396 °C. Both Cu-K/γ-Al_2O_3 and Cu-La/γ-Al_2O_3 catalysts had better catalytic activities than Cu/γ-Al_2O_3 catalyst, which increased greatly with an increase in the reaction temperature. Cu-K-La/γ-Al_2O_3 catalyst had the best catalytic activity among the above-mentioned copper-based catalysts, in which when the reaction temperature was higher than 360 °C, the conversion of HCl reached the similar value of about 86% due to the thermodynamic-controlled Deacon reaction at higher reaction temperatures. These results indicate that the significant increase in the catalytic activity of Cu-K-La/γ-Al_2O_3 catalyst is due to the synergistic promotion effect of KCl and $LaCl_3$.

Fig. 2 shows the effect of the total loading amount of the chloride precursors ($CuCl_2$, KCl and $LaCl_3$) on the conversion of HCl over Cu-K-La/γ-Al_2O_3 catalyst for HCl oxidation. As shown in Fig. 2, with an increase in the total loading amount of the chloride precursors,

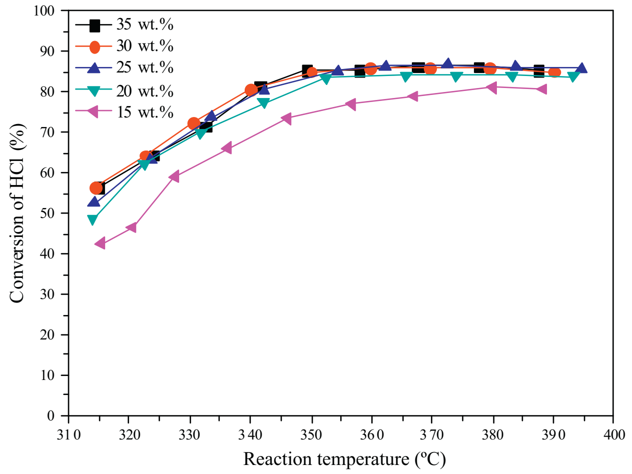

Fig. 2. Effect of the total loading amount of the chloride precursors on the conversion of HCl over Cu-K-La/γ-Al_2O_3 catalyst for HCl oxidation.