‘Ethane oxychlorination’ over $\gamma$-Al$_2$O$_3$ supported CuCl$_2$–KCl–LaCl$_3$

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A study on $\gamma$-Al$_2$O$_3$ supported CuCl$_2$–KCl–LaCl$_3$ for ethane oxychlorination was carried out by means of XRD, XPS, TGA/DTA, BET TEM and ICP. The experimental results indicate that the catalytic properties of the 5 wt.%Cu–6 wt.%K–5 wt.%La/$\gamma$-Al$_2$O$_3$ are optimal. This catalyst was studied in more detail and it was found that deactivation of the catalyst was due to carbon deposition and loss of active species of Cu$^{+2}$.

KEY WORDS: ethane; oxychlorination; ethylene chloride.

1. Introduction

Copper chloride has been a typical catalyst for oxychlorination reaction of hydrocarbon. Since the discovery that copper chloride catalyzes the conversion of hydrogen chloride to chlorine in the Deacon process, much work has been done on the oxychlorination reaction of methane and ethylene [1–4]. However, ethane oxychlorination is promising for developing a rational technology of ethylene chloride production, because ethane as a raw material is cheaper than ethylene [5,6]. Despite the different temperature ranges in which these reactions are carried out: 473–573 K for ethylene oxychlorination, 623–723 K for the methane oxychlorination, and 723–773 K for ethane oxychlorination, the same promoters (potassium chloride and rare-earth chloride) are usually considered to show the same function for these reactions. One of the roles played by the rare-earth elements is to prevent agglomeration. In an electron microscopic study of copper chloride–potassium chloride mixtures supported on low area Al$_2$O$_3$ and TiO$_2$, the mobility of clusters leading to agglomeration at temperatures above 673 K was observed [7], upon addition of rare-earth elements the catalysts showed a decreasing tendency to agglomerate.

The purpose of this work is to investigate effect of lanthanum on the catalytic activity and selectivity for ethane oxychlorination and to illuminate the reason for the deactivation of the above-mentioned optimal catalyst after reaction for 100 h.

2.1 Experimental

2.1. Catalysts preparation and characterization

Commercial $\gamma$-Al$_2$O$_3$ (specific surface area: 200 m$^2$/g, pore volume: 0.37 cm$^3$/g) was chosen as the support. An aqueous solution containing CuCl$_2$·2H$_2$O, KCl and LaCl$_3$ was used to impregnate the support by an incipient wetness method. The samples were dried at 393 K in air for 2 h, followed by calcination in a muffle furnace at 823 K for 4 h. The prepared catalysts were stored in a desiccator.

Same content of 5 wt.% copper and 6 wt.% potassium and variable contents 0, 1, 3, 5, 7 and 9 wt.% of lanthanum are adopted for preparation of the series of catalysts [8], which are denoted as CuKXLa, Where X represents weight percentage of La, for example, CuK3La stands for a catalyst containing 5 wt.% Cu, 6 wt.% K and 3 wt.% La.

XRD patterns of this series of catalysts were collected at room temperature by a Shimadzu XRD-6000 X-ray powder diffractometer using Ni-filtered Cu K$\alpha$ radiation at 40 kV and 30 mA in a 2$h$ range of 10–80 at a scanning rate of 4$/min$.

The oxidation states of copper before and after the reaction were characterized by X-ray photoelectron spectroscopy(XPS; VG ESCA Mark II) using AlK$\alpha$ radiation.

TGA/DTA technique was utilized to investigate the weight loss and the thermal transformations of the catalysts. The amount of carbon deposited on the catalysts was determined using a thermo-gravimetric analyzer (TGA; Perkin-Elmer TGA7) and a differential thermal analyzer (DTA; Perkin-Elmer DTA 1700).

The measurements of the specific surface area of the catalysts were conducted by BET method on MICROMERITICS ASAP-2012 using nitrogen as adsorbate at liquid nitrogen temperature.

Transmission electron microscopic (TEM) images of the catalysts were obtained using a HITACHI-8100IV electron microscope operated at 200 KV. The catalysts were ground in an agate mortar and suspended in cyclohexane [9]. After ultrasonic dispersion one drop of the sample suspension was mounted on a copper grid.

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ICP determinations of the catalysts were made using a PLASMA ICP-1000 spectrometer.

2.2 Catalytic properties test

The catalytic properties of the catalysts for the topic reaction were tested in a tubular fixed-bed continuous flow quartz reactor. A thermocouple was placed in the center of the catalyst bed to monitor the reaction temperature. The reactant mixture consisted of \( \text{C}_2\text{H}_6 \), \( \text{HCl} \) and air at a volume ratio of \( \text{C}_2\text{H}_6 : \text{HCl} : \text{air} = 1:3:5 \) and a total flowrate of 36 ml/min was used. 1 g catalyst was used in each run. The catalyst was pre-treated in an HCl–air mixture at 773 K for 30 min [10]. The reaction were run at 773 K.

3. Results and discussion

3.1. Catalytic properties for ethane oxychlorination

Data for lanthanum content dependence of ethane conversion at 773 K are shown in figure 1, indicating that the conversion of ethane first tends to decrease, then increases with an increase in concentration of lanthanum. Over a catalyst containing 5 wt.% lanthanum (\( \text{CuK5La} \)), the conversion of ethane reaches a maximum. figure 2 shows the influence of lanthanum on the selectivity and yield of ethylene. It is worth to note that the selectivity and yield of ethylene over the \( \text{CuK5La} \) catalyst are lower than that over the others, but the selectivity for ethylene chloride is optimal (figure 3). The sum of the ethylene yield and ethylene chloride yield over this catalyst is almost unchanged with the concentration of lanthanum, implying that there is a competition between formations of the ethylene and ethylene chloride. The \( \text{CuK5La} \) catalyst shows the highest ethane conversion and ethylene chloride selectivity. We have investigated the initial activity and stability of the \( \text{CuK5La} \) catalyst, found that no deactivation is detected within 100 h of time on stream over it. The conversion of ethane changes in a fluctuating mode between 88 and 92% and the sum of ethylene selectivity and ethylene chloride selectivity is higher than 70% (figures 4 and 5). The yield of ethyl chloride and 1,2-dichloroethane and carbon oxides increase gradually.

The catalytic process for the oxidative chlorination of ethane may be represented as follows [10]:

The reaction scheme suggests that the rate of oxidation increases and the rate of the dehydrochlorination of these compounds decreases. The used \( \text{CuK5La} \) catalyst can simply be regenerated in HCl and air atmosphere at 773 K and its catalytic properties can be recovered.

Turnover rate (TR) of ethane in it oxychlorination was calculated based on the data for ethane conversion, total flowrate of the reactant, ICP determination and XPS measurement. In this calculation, we referred to reference [11] the authors of which indicated that only highly dispersed anhydrous \( \text{CuCl}_2 \) is active for this.

![Figure 1. Influence of content of La on the conversion of ethane.](image1)

![Figure 2. Influence of content of La on the yield and selectivity of \( \text{C}_2\text{H}_4 \).](image2)

![Figure 3. Influence of content of La on the yield and selectivity of \( \text{C}_2\text{H}_3\text{Cl} \).](image3)