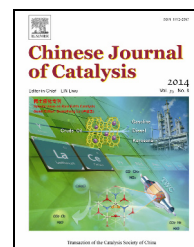


available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Rare Earth Catalysis)

Effect of KCl on the performance of Cu-K-La/ γ -Al₂O₃ catalyst for HCl oxidation

Kanka Feng^a, Chenwei Li^a, Yanglong Guo^{a,*}, Wangcheng Zhan^a, Binqun Ma^b, Binwu Chen^b, Maoquan Yuan^b, Guanzhong Lu^{a,#}

^a Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, China

^b Shanghai Chlor-Alkali Chemical Co., Ltd., Shanghai 200241, China

ARTICLE INFO

Article history:

Received 1 May 2014

Accepted 13 June 2014

Published 20 August 2014

Keywords:

Hydrogen chloride

Catalytic oxidation

Chlorine

Copper-based catalyst

Potassium chloride

ABSTRACT

Cu-K-La/ γ -Al₂O₃ catalysts prepared by the incipient wetness impregnation for the catalytic oxidation of HCl to Cl₂ at atmospheric pressure were investigated for the effect of KCl on the catalyst performance. Cu-K-La/ γ -Al₂O₃ catalyst with 5 wt% KCl loading showed good activity and stability due to the promotion by KCl. It gave good activity over a wide range of space velocity of the feed gas and conversion of HCl above 85%, and it was nearly unchanged in activity after 100 h reaction at the conditions of 0.1 MPa, 360 °C, space velocity of 450 L/(kg-cat·h), and HCl/O₂ molar ratio = 2:1. X-ray diffraction results indicated that Cu, K, and La species were highly dispersed on the surface of the γ -Al₂O₃ support. H₂ temperature-programmed reduction results indicated that the addition of KCl favored the reduction of Cu²⁺ to Cu⁺ and improved the activity of the active sites of Cu²⁺ species for HCl oxidation.

© 2014, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Chlorine has many applications as disinfectant, purifier, and a raw material for manufacturing important monomers (toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and vinyl chloride), solvents, agrochemicals, pharmaceuticals, and so on. In the processes for manufacturing these products, HCl is formed as a byproduct. Moreover, in the manufacture of TDI or MDI, the byproduct of HCl is four times the molar amounts of TDI and MDI. The demands for TDI and MDI are increasing sharply, which will result in the inevitable produc-

tion of more HCl than its market demand, and the serious disposal problem of a toxic waste and not meeting increasingly stringent environmental regulations. Therefore, it is necessary and urgent to recycle chlorine in chlorine-related industries [1,2].

Although the catalytic oxidation of HCl to chlorine by air or O₂ (so-called Deacon process) has been known for over 140 years [3], the Deacon process is limited by general disadvantages such as fast deactivation of the catalyst due to the volatilization of the catalytic metals in the form of chlorides, and severe corrosion issues caused by unreacted HCl and H₂O

* Corresponding author. Tel/Fax: +86-21-64252923; E-mail: ylguo@ecust.edu.cn

Corresponding author. Tel/Fax: +86-21-64252923; E-mail: gzhlu@ecust.edu.cn

This work was supported by the National Basic Research Program of China (973 Program, 2010CB732300), Commission of Science and Technology of Shanghai Municipality (13521103402), and Shu Guang Project of Shanghai Municipal Education Commission and Shanghai Education Development Foundation (10SG30).

DOI: 10.1016/S1872-2067(14)60166-2 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 35, No. 8, August 2014

product [1]. Therefore, the Deacon process has been largely replaced by the electrolysis of HCl, but this has the disadvantage of high electricity consumption. In recent years, some breakthroughs in chlorine production from the catalytic oxidation of HCl have been achieved over Ru-based catalysts, namely, RuO₂/rutile-TiO₂ catalyst by Sumitomo [4] and RuO₂/SnO₂-Al₂O₃ catalyst by Bayer [5,6]. However, Ru is a noble metal and its market price is expensive and highly fluctuating (<http://www.platinum.matthey.com/prices/price-charts>) [2], which will limit the large scale industrialization of Ru-based catalysts. The Deacon process has attracted increasing attention because of its relative ease of operation and lower energy consumption and thermal requirements. Therefore more efforts have focused on developing efficient Cu-based catalysts [7–9] and other effective catalysts with lower costs to replace the expensive Ru-based catalysts [10–14].

In our previous work, an efficient Cu-K-La/ γ -Al₂O₃ catalyst was developed for the catalytic oxidation of HCl to chlorine [15]. The conversion of HCl was 75%–82% and the average conversion of HCl was 78% for a reaction of over 9600 h under the reaction conditions of 0.1 MPa, 340 °C, space velocity of 450 L/(kg-cat·h), and HCl/O₂ molar ratio = 2:1. A demonstration plant of 1000 ton/year of chlorine from the catalytic oxidation of HCl is under construction. The aims of this work are to investigate the effect of KCl on the catalytic performance of the Cu-K-La/ γ -Al₂O₃ catalyst for HCl oxidation and explore the promotion mechanism of KCl.

2. Experimental

2.1. Preparation of catalyst

The Cu-K-La/ γ -Al₂O₃ catalysts were prepared by the incipient wetness impregnation method in our previous work [15], in which the loadings of CuCl₂ and LaCl₃ were 15 and 10 wt%, respectively. The mass ratios of KCl to CuCl₂ were 0, 1/6, 1/3, 1/2, 2/3, and 1, respectively.

2.2. Characterization of the Cu-K-La/ γ -Al₂O₃ catalyst

Powder X-ray diffraction patterns were recorded on a Bruker AXS D8 Focus diffractometer operated at 40 kV, 40 mA (Cu K α radiation, λ = 0.15406 nm). The diffraction patterns were measured in the range of 10° < 2 θ < 80° at a scanning rate of 6°/min. Elemental analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a TJA IRIS ADVANTAG 1000 instrument. H₂ temperature-programmed reduction experiments were carried out in a flow system equipment with a TCD detector. Sample (100 mg) was loaded into the quartz tube reactor which then was heated from 100 to 800 °C at the rate of 10 °C/min in an atmosphere of 5% H₂/N₂ at 45 mL/min.

2.3. Catalytic oxidation of HCl

The catalytic oxidation of HCl over the Cu-K-La/ γ -Al₂O₃ catalysts was investigated in a quartz fixed-bed reactor under the

reaction conditions of 30 g catalyst, 0.1 MPa, space velocity of 450 L/(kg-cat·h), and HCl/O₂ = 2:1 (molar ratio). The flow rates of HCl and O₂ were 150 and 75 mL/min, respectively, which were fed into the reactor by mass flow controllers. The product of chlorine was analyzed by the iodometry method and the unreacted HCl was quantified by a standard NaOH solution. There was no byproduct in the catalytic oxidation of HCl, hence the selectivity for chlorine was 100% and the conversion of HCl was equal to that of the yield of chlorine.

3. Results and discussion

3.1. Effect of the mass ratio of KCl/CuCl₂

Figure 1 shows the effect of the mass ratio of KCl/CuCl₂ on the conversion of HCl over the Cu-K-La/ γ -Al₂O₃ catalysts for HCl oxidation. The mass ratio of KCl/CuCl₂ had a significant influence on the conversion of HCl. The conversion of HCl increased significantly with increasing mass ratio of KCl/CuCl₂ up to 1/3, and the conversions of HCl were almost the same over Cu-K-La/ γ -Al₂O₃ catalysts with the mass ratio of KCl/CuCl₂ of 1/6 and 1/3. When the reaction temperature was higher than 360 °C, the conversions of HCl were similar over the Cu-K-La/ γ -Al₂O₃ catalysts with the mass ratios of KCl/CuCl₂ of 1/6 and 1/3. The Deacon process is an exothermic reaction, and a lower reaction temperature is favorable for increasing the equilibrium conversion. The Deacon process is a kinetics-controlled reaction at lower temperatures and a thermodynamics-controlled reaction at higher temperatures [16]. However, with further increasing of the mass ratio of KCl/CuCl₂, the active sites of Cu²⁺ species were partly covered by K species, which resulted in an obvious decrease in the conversion of HCl to be even lower than that of the catalyst without the addition of KCl.

3.2. Effect of space velocity of feed gas

Figure 2 shows the effect of the space velocity of the feed gas

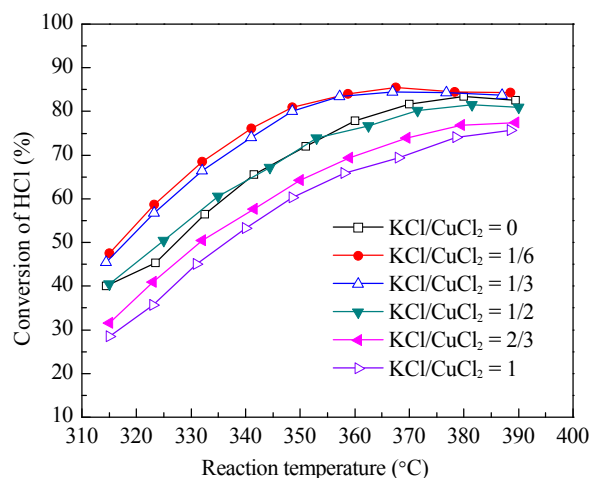


Fig. 1. Effect of the mass ratio of KCl/CuCl₂ on the conversion of HCl over Cu-K-La/ γ -Al₂O₃ catalysts for HCl oxidation. Reaction conditions: 30 g catalyst, 0.1 MPa, space velocity of 450 L/(kg-cat·h), HCl/O₂ molar ratio = 2:1.

Download English Version:

<https://daneshyari.com/en/article/60067>

Download Persian Version:

<https://daneshyari.com/article/60067>

[Daneshyari.com](https://daneshyari.com)