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

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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.

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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

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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 on the conversion of HCl over the Cu-K-La/ γ -Al₂O₃ catalyst with

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.

Fig. 2. Effect of the space velocity of the feed gas on the conversion of HCl over a Cu-K-La/ γ -Al₂O₃ catalyst for HCl oxidation. Reaction conditions: 30 g catalyst, 0.1 MPa, 360 °C, HCl/O₂ molar ratio = 2:1.

the mass ratio of KCl/CuCl₂ of 1/3. The decline rate of the conversion of HCl became slower with increasing space velocity of the feed gas. When the space velocity of the feed gas was increased from 150 to 450 L/(kg-cat·h), the conversion of HCl was decreased from 94.5% to 86.6%. However, on further increasing the space velocity of the feed gas from 450 to 750 L/(kg-cat·h), the conversion of HCl only decreased from 86.6% to 83.9%. An increase in the space velocity of the feed gas decreased the residence time of HCl on the catalyst surface and hence resulted in a decrease in the conversion of HCl. Therefore the Cu-K-La/ γ -Al₂O₃ catalyst showed good catalytic activity over a wide range of the space velocity of the feed gas.

3.3. Catalyst stability

Figure 3 shows the stability of the Cu-K-La/ γ -Al₂O₃ and Cu-La/ γ -Al₂O₃ catalysts with 5 wt% KCl loading for HCl oxidation for 100 h. It was found that the conversion of HCl was kept above 85% and remained little change for 100 h. After reaction for different times, the water product was collected for 5 h and then ICP-AES was used for the evaluation of the loss of Cu from the Cu-K-La/ γ -Al₂O₃ catalyst. The loss of Cu at the sampling

Fig. 3. Stability of Cu-K-La/ γ -Al₂O₃ and Cu-La/ γ -Al₂O₃ catalysts for HCl oxidation. Reaction conditions: 30 g catalyst, 0.1 MPa, 360 °C, space velocity of 450 L/(kg-cat·h), HCl/O₂ molar ratio = 2:1.

points of reaction times for 55 and 100 h were 5.5×10^{-7} and 3.5×10^{-7} g/h, respectively, which indicated that the loss of Cu was negligible. However, over the Cu-La/ γ -Al₂O₃ catalyst, the initial conversion of HCl was 80% and it declined gradually after reaction for 62 h. Therefore the Cu-K-La/ γ -Al₂O₃ catalyst showed better activity and stability due to the promotion by KCl.

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

3.4.1. XRD results

Figure 4 shows the XRD patterns of the Cu-K-La/ γ -Al₂O₃ catalysts with different mass ratios of KCl/CuCl₂. When the mass ratios of KCl/CuCl₂ were lower than 2/3, there were only the broad characteristic diffraction peaks of the γ -Al₂O₃ (JCPDS No. 10-0425) support at $2\theta = 37.6^\circ$, 45.9° , and 67.1° , and the characteristic diffraction peaks of Cu, K, and La species were not observed, which indicated that they were highly dispersed on the surface of the γ -Al₂O₃ support. With an increase in the mass ratio of KCl/CuCl₂, the intensities of the diffraction peaks of the γ -Al₂O₃ support decreased gradually. With increasing of the mass ratio of KCl/CuCl₂ to 2/3 above, the characteristic diffraction peaks of KCl were observed at $2\theta = 28.3^\circ$, 40.6° , and 50.8° , which indicated that a small amount of K species existed in the form of KCl nanocrystals.

3.4.2. H₂-TPR results

Figure 5 shows the H₂-TPR profiles of the Cu-K-La/ γ -Al₂O₃ catalysts with different mass ratios of KCl/CuCl₂. There were two obvious reduction peaks over all the Cu-based catalysts, which were attributed to the step reduction of Cu²⁺ → Cu⁺ → Cu⁰. With increasing the mass ratio of KCl/CuCl₂ from 1/6 to 1, the peak temperature of the reduction peak of Cu²⁺ to Cu⁺ increased from 308 to 352 °C.

Combining with the results in Fig. 1, the trend of the mass ratio effect on the conversion of HCl was the same as on the

Fig. 4. XRD patterns of Cu-K-La/ γ -Al₂O₃ catalysts with different mass ratios of KCl/CuCl₂.

Fig. 5. H_2 -TPR profiles of Cu-K-La/ γ - Al_2O_3 catalysts with different mass ratios of KCl/ CuCl_2 .

peak temperature of the reduction peak of Cu^{2+} to Cu^+ , in which the lower temperature of the reduction of Cu^{2+} to Cu^+ was favorable for increasing the catalytic activity of the active sites of Cu^{2+} species. Therefore, the addition of KCl favored the reduction of Cu^{2+} to Cu^+ and thus improved the catalytic activity for HCl oxidation. These findings are similar to those reported by Rouco et al. [17] for low temperature ethylene oxyhydrochlorination over CuCl_2 -based catalysts.

4. Conclusions

The addition of KCl improved the activity and stability of Cu-K-La/ γ - Al_2O_3 catalyst for HCl oxidation. The conversion of HCl was kept above 85% and nearly unchanged for 100 h over Cu-K-La/ γ - Al_2O_3 catalyst with 5 wt% KCl loadings under the reaction conditions of 0.1 MPa, 360 °C, space velocity of 450 L/(kg-cat·h), and HCl/ O_2 molar ratio = 2:1. The results showed

that Cu, K, and La species were highly dispersed on the support surface; the addition of KCl promoted the reduction of Cu^{2+} to Cu^+ and thus improved the activity of the active sites of Cu^{2+} species for HCl oxidation.

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Graphical Abstract

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Addition of KCl improved the activity of the active sites of Cu^{2+} species and the stability of Cu-K-La/ γ - Al_2O_3 catalyst for HCl oxidation.

Copper-based catalyst

KCl 对 Cu-K-La/ γ -Al₂O₃ 催化剂上 HCl 氧化反应性能的影响

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摘要: 采用等体积浸渍法制备了Cu-K-La/ γ -Al₂O₃催化剂, 考察了KCl对该催化剂催化HCl氧化制Cl₂反应性能的影响. 当KCl的负载量为5 wt%时, Cu-K-La/ γ -Al₂O₃催化剂表现出较好的催化活性和稳定性, 可在较大的原料气空速变化范围内使用. 在0.1 MPa, 360 °C, 空速450 L/(kg-cat·h)和HCl/O₂摩尔比为2:1的反应条件下, Cu-K-La/ γ -Al₂O₃催化剂上HCl转化率在100 h内保持85%以上. 表征结果表明, Cu, K和La物种均高度分散于 γ -Al₂O₃载体表面; 一定量KCl的加入可降低Cu²⁺ → Cu⁺的还原温度, 从而提高Cu²⁺活性中心的催化活性.

关键词: 氯化氢; 催化氧化; 氯气; 铜基催化剂; 氯化钾

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