Applied Catalysis A: General 365 (2009) 20–27

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Composition optimization of silica-supported copper (II) chloride substance for phosgene production

Tianzhu Zhang [a,c,*], Carsten Troll [a], Bernhard Rieger [a,**], Juergen Kintrup [b],
Oliver F.-K. Schlüter [b], Rainer Weber [b]

[a] WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenburgstraße 4, 85747 Garching, Germany
[b] Bayer MaterialScience AG, 51373 Leverkusen, Germany
[c] State Key Lab of Bioelectronics, Jiangsu Key Lab for Biomaterials and Devices, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, China

ARTICLE INFO

Article history:
Received 10 April 2009
Received in revised form 4 May 2009
Accepted 6 May 2009
Available online 13 May 2009

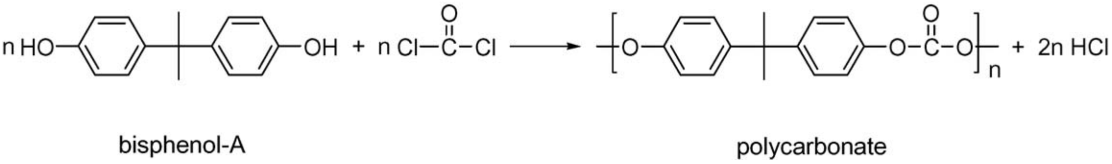
Keywords:
Oxychlorination
IR
Carbon monoxide
Phosgene
Hydrogen chloride
Silica gel

ABSTRACT

In this work, we checked the influences of the silica-supported copper (II) chloride substance composition on the oxychlorination of CO to phosgene. The effects of the content of copper (II) chloride, the ratio of copper to potassium, the different kinds of promoters, like sodium chloride, potassium chloride and caesium chloride, and the surface area of silica gel were systematically investigated. The lower surface area of the support can contribute to the formation of phosgene while the higher surface area of the support can lead to a rather low yield of phosgene. The reaction activity of silica-supported copper (II) chloride substance increases with the content of copper chloride (within 30 wt.%). However, in order to avoid the agglomeration of the substance, the content of copper chloride should be less than 30 wt.%. The optimized molar ratio of $CuCl_2$ to KCl is 5:1. Of all three promoters, NaCl, KCl and CsCl, CsCl or KCl can function better than NaCl due to the stronger Lewis basicity. The molten phase can remarkably improve the contact of $CuCl_2$ and CO. On the whole, the lower-surface-area support, the higher content of $CuCl_2$ and the promoter CsCl or KCl are prefered in the oxychlorination of CO.

1. Introduction

Numerous chlorination or phosgenation processes through the elemental chlorine (Cl_2) as a raw material and many metallurgical processes produce a large amount of toxic and corrosive hydrogen chloride (HCl) streams. Especially, with the rapidly increasing demand for polyurethanes and polycarbonates today [1,2], more and more Cl_2 or phosgene ($COCl_2$) is consumed and consequently more and more by-product HCl is produced. For example, in the production of bisphenol A polycarbonates, $COCl_2$ is degraded to HCl (Eq. (1)).



(1)

At present, about 95% of all chlorine is produced by the electrolysis of brine called the chloralkali process, only a small amount of Cl_2 is produced through the catalytic oxidation of HCl (Deacon reaction) [3,4]. Further, about 14% of chlorine is used to produce phosgene through reacting with CO catalyzed by the activated charcoal. On the one hand, this electrochemical method is rather electricity-consuming [5,6]; on the other hand, the amount of caustic soda which is formed together with chlorine is much larger than its demand, which is undesirable [7–10]. The production of Cl_2 or phosgene and recycling of HCl will face a new and huge challenge. To effectively fulfill the

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* Corresponding author at: State Key Lab of Bioelectronics, Jiangsu Key Lab for Biomaterials and Devices, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, China. Tel.: +86 25 83272476;
fax: +86 25 83272460.
** Corresponding author. Tel.: +49 89 28913570; fax: +49 89 28913562.
E-mail addresses: zhangtianzhuglq@yahoo.com.cn (T. Zhang), rieger@tum.de (B. Rieger).

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doi:10.1016/j.apcata.2009.05.006

recycle of HCl in the industrial production is rather pressing and necessary at present.

A lot of effort has been continuously done in developing more efficient methods for recycling HCl in the industrial production out of consideration for economic and environmental reasons [11–16].

There are two main routes to recycle by-product HCl. One route is the above mentioned Deacon-type reaction to directly recycle HCl to chlorine (Eq. (2)). Another one is the oxychlorination of CO to phosgene from HCl and air (Eq. (3)).

$$HCl + 1/4O_2 \rightleftharpoons 1/2Cl_2 + 1/2H_2O \tag{2}$$

$$CO + 1/2O_2 + 2HCl \rightarrow COCl_2 + H_2O \tag{3}$$

Some efficient processes were developed to produce Cl_2 from HCl, such as Shell-Chlor process ($CuCl_2$–KCl/SiO_2 catalyst) (Shell company, Netherlands) [17–20], MT-Chlor process (Cr_2O_3/SiO_2 catalyst) (Mitsui Toatsu company, Tokyo, Japan) [21–23] and Sumitomo process (RuO_2/TiO_2 catalyst) (Sumitomo Chemicals, Tokyo, Japan) [24,25].

Many companies also developed other attractive processes to directly prepare phosgene from CO, HCl and air and therefore to recycle HCl.

For example, in 1948, Socony-Vacuum Oil Company invented a continuous process for the production of phosgene from carbon monoxide, hydrogen chloride and air catalyzed by copper chloride, which includes two major steps, namely the oxidation–neutralization step and the chlorination step [26]. One of the major advantages of this method is that by-product HCl can be directly recycled to phosgene. This process paved a new way to the effective recycle of HCl in the production of phosgene. However, because of problems with the corrosion and catalyst vaporization, this catalytic process obtained only a limited industrial application.

In 1973, Rhone-Progil made a further improvement in this two-step process for the production of phosgene from CO, HCl, air and copper chloride [27]. The type and surface area of the supports and the atomic ratio of Cu:K were optimized. The lower surface area of support can contribute to a higher yield of phosgene. The support silica is better than alumina or magnesia. In 1982, The Lummus Company improved the first step through using the molten salts mixture of cuprous and cupric chlorides to enrich the salts in the higher valent metal chlorides [28].

In 1984, Ryan et al. systematically investigated the reaction mechanism of oxychlorination of CO to phosgene and the effect of the catalyst composition on the catalyst activity and reaction selectivity [29]. However, the oxychlorination of CO was carried out with a one-pot method, where CO, HCl and air were simultaneously stoichiometrically fed to the reactor charged with copper chloride as the catalyst. The maximum selectivity of phosgene formation is only 57.2% with a conversion of carbon monoxide corresponding to 42%, and a lot of carbon dioxide was formed together. In addition, it is rather difficult to identify the key factors that have a major influence on the reaction results.

In 1997, Young & Basile, P.C. invented another process for the production of phosgene comprising the following two steps operated in tandem: (1) perchloroethylene $CCl_2{=}CCl_2$ reacts first with HCl and O_2 to form hexachloroethane catalyzed by the oxychlorination catalyst; (2) then hexachloroethane CCl_3CCl_3 continues to react with CO to produce phosgene catalyzed by the activated carbon [30]. In fact, $CuCl/CuCl_2$ catalyst system was replaced with $CCl_2{=}CCl_2/CCl_3CCl_3$ compared with the processes reported by Refs. [28,29]. Although the reaction temperature is decreased to some extent, the process is not practical due to the higher volatility of $CCl_2{=}CCl_2/CCl_3CCl_3$ compared with $CuCl/CuCl_2$.

Therefore the major research is still focused on the $CuCl/CuCl_2$ catalyst system so far. In order to understand the reaction mechanism and further improve Deacon-type reactions, a lot of studies are correspondingly focused on the characterization of the Cu centers with different techniques such as XRD, EDX, EPR, UV–vis DRS, IR, EXAFS, XANES and so on [31–48].

However, the previous investigations are very limited and not enough; the detailed information of catalytic reaction mechanism is rather little known. Therefore, further research is still needed.

In our recent work, the kinetics of oxychlorination of carbon monoxide was investigated and reaction conditions (temperature, contact time and pressure of carbon monoxide) were optimized [49]. In order to improve this oxychlorination of carbon monoxide, the catalyst composition needs to be optimized further. When used in the separated stage, the substances containing copper chloride will be present in stoichiometric quantities and are not qualified as catalysts. In the present study, more defined and fixed reaction conditions were set and the effects of substance containing copper chloride composition upon the reaction activity, the formation rate and the yield of phosgene were systematically probed.

2. Experiment

2.1. Apparatus

The experimental setup can be referred to Ref. [49].

2.2. Preparation of silica-supported copper (II) chloride substances

The silica-supported copper (II) chloride substances were prepared by the incipient-wetness technique [34,49]. Two different kinds of silica gel were used here. SiO_2-1: surface area 25 $m^2\,g^{-1}$, average pore diameter 150 nm, pore volume 0.9 mL g^{-1}, particle size 90–130 μm; SiO_2-2: surface area 320 $m^2\,g^{-1}$, average pore diameter 15 nm, pore volume 1.2 mL g^{-1}, particle size 100–300 μm.

The prepared silica-supported copper (II) chloride substances are formulated in terms of $CuCl_2$ content, the molar ratio of $CuCl_2$ to promoter and the type of support. For example, 20Cu:4K/SiO_2-1 refers to a SiO_2-1-supported mass containing 20 wt.% $CuCl_2$ with the molar ratio of 20:4 ($CuCl_2$:KCl).

2.3. SEM measurements

The scanning electron microscopy (SEM) experiments were conducted on a Hitachi TM-1000 instrument operated at 200 kV.

2.4. Extraction experiments

200 mg fresh silica-supported copper (II) chloride substance was added to 20 mL ethanol (CP grade) in a 50-mL round-bottom flask. The mixture was stirred at room temperature for 30 min and then filtered. The residual was washed with 5 mL ethanol. Finally, a 25 mL extraction solution was obtained. Quantitative analysis of Cu in the extraction solutions was performed with a Varian CARY 3 UV-visible Spectrophotometer.

2.5. Reaction of silica-supported $CuCl_2$ with CO

$$CO + 2CuCl_2 \rightarrow COCl_2 + 2CuCl \tag{4}$$

5 bar CO (4.7 mmol) was fed to the autoclave charged with the fresh silica-supported copper (II) chloride substance (including 0.5 mmol $CuCl_2$) at 300 °C (unless specified in other place). The reaction time is 6 min. Following the above reaction conditions, the silica-supported copper (II) chloride substance was continuously used several times until all active $CuCl_2$ was depleted (Eq. (4)).