Journal of Catalysis 270 (2010) 76–85

Contents lists available at ScienceDirect

Journal of Catalysis

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

Oxychlorination of CO to phosgene in a three-step reaction cycle and corresponding catalytic mechanism

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ARTICLE INFO

Article history:
Received 31 October 2009
Revised 7 December 2009
Accepted 8 December 2009
Available online 6 January 2010

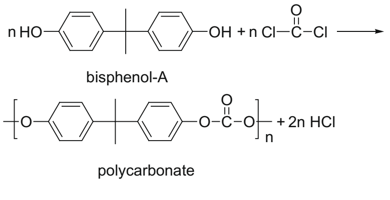
Keywords:
Oxychlorination
Three-step procedure
Regeneration
Oxidation
Neutralization
Phosgene

ABSTRACT

An improved procedure, three-step reaction cycle procedure, for the continuous preparation of phosgene from CO, air and HCl catalyzed by $CuCl_2$ was reported for the first time. The corresponding catalytic mechanism of each step was preliminarily disclosed with the powder X-ray diffraction (XRD) analysis: the first step is the oxychlorination of CO to phosgene and simultaneous reduction of $CuCl_2$ to CuCl; the second step is the oxidation of CuCl with air to Cu_2OCl_2, and the third step is the neutralization of Cu_2OCl_2 with HCl to $CuCl_2$. The regeneration of catalyst consists of steps 2 and 3, which is called the two-step regeneration of catalyst. The no-simultaneous existence of Cu (I) chloride and water in this three-step reaction procedure prevented effectively copper (I) chloride from the disproportionation. The influence of regeneration conditions, including reaction time, pressure of air or HCl on morphologies and recovery degree of catalyst were investigated and discussed. The degree of recovery for the single-run yield and cumulative yield of phosgene from the two-step regenerated oxychlorination agent can reach, respectively, 87.0% and 97.0% whereas the single-run yield and cumulative yield of phosgene with the one-step regenerated catalyst only can be recovered to 58.8% and 80.5%, respectively. The two-step regeneration method also can result in a higher dispersion of $CuCl_2$/KCl on silica gel than that of the one-step regeneration. These results not only can offer a quite promising potential for the industrial use, but also can promote our deeply understanding of this important industrial reaction.

1. Introduction

Numerous chlorination or phosgenation processes through elemental chlorine (Cl_2) as a raw material and many metallurgical processes produce a large amount of toxic and corrosive hydrogen chloride (HCl) stream. Especially, with the rapidly increasing demand for polyurethanes (PU) and polycarbonates (PC) today [1–3], more and more Cl_2 or phosgene ($COCl_2$) was consumed, and consequently more and more by-product HCl was produced.



(1)

For example, in the production of bisphenol A polycarbonates, $COCl_2$ was degraded to HCl (Eq. (1)). The production of Cl_2 or phosgene and recycling of HCl will face a new and huge challenge.

At present, the main Cl_2 production method is still the electrolysis of aqueous solution of sodium chloride, only a small amount of Cl_2 is produced through the catalytic oxidation of HCl (Deacon reaction) [4,5]. However, the electrolytic process has still its own problems. On the one hand, this electrochemical method is rather electricity-consuming [6,7]; on the other hand, the amount of caustic soda, which was formed together with chlorine is much larger than its demand [8–11]. To effectively fulfill the recycle of HCl in the industrial field is rather pressing and necessary. Therefore, a large number of researchers are gradually switching their interests again to the catalytic oxidation of HCl or oxychlorination of CO for the production of Cl_2 or $COCl_2$ out of consideration for economic and environmental reasons [12–17]. A lot of effort has been continuously done in finding more efficient methods for recycling HCl by converting HCl into Cl_2 or the relevant chemicals, such as $COCl_2$.

Some efficient systems were developed to produce Cl_2 from HCl (Eq. (2)), such as Shell-Chlor process ($CuCl_2$–KCl/SiO_2 catalyst) (Shell Company, Netherlands) [18], MT-Chlor process (Cr_2O_3/SiO_2

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doi:10.1016/j.jcat.2009.12.008

catalyst) (Mitsui Toatsu Company, Tokyo, Japan) [19,20] and Sumitomo process (RuO_2/TiO_2 catalyst) (Sumitomo Chemicals, Tokyo, Japan) [21].

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

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 chlorination step (Eq. (3)) and the oxidation–neutralization step (Eq. (4)) [22]. 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 for the production of phosgene. However, because of problems with the corrosion and catalyst vaporization, this catalytic process obtained only a limited industrial application.

$$2CuCl_2 + CO \rightarrow COCl_2 + 2CuCl \tag{3}$$

$$2CuCl_2 + 2HCl + 1/2O_2 \rightarrow 2CuCl_2 + H_2O \tag{4}$$

In 1973, Rhone-Progil declared an improved process for the production of phosgene from CO, HCl, air and copper chloride in two steps: (1) HCl/air (ratio of volume is 0.7) was introduced to the reactor at 400 °C first to ensure all Cu (I) was converted to Cu (II); (2) after cleaning with nitrogen CO was fed at 350 °C to produce phosgene. The oxychlorination of CO and the regeneration of catalyst were carried out in two completely separated stages. Therefore, phosgene can be formed at lower temperatures, and the amount of CO_2 and Cl_2 was reduced. The problem with the corrosion and hydrolysis of phosgene can be overcome. In this process, the composition of catalyst was also optimized [23]. In 1982, Lummus Company improved the first step through using a mixture of molten cuprous and cupric chlorides to enrich the salt in the higher valent metal chloride [24].

In order to understand the reaction mechanism and improve further Deacon-type reactions, a lot of studies are correspondingly focused on the characterization of the Cu centers with different techniques, such as powder X-ray diffraction (XRD), energy-dispersive X-ray (EDX), electron paramagnetic resonance (EPR), Ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DRS), Fourier transform infrared (FT-IR), extended X-ray absorption fine structure spectroscopy (EXAFS), X-ray absorption near edge structure spectroscopy (XANES) [25–33]. The detailed information of catalytic reaction mechanism is still rather little known [34,35].

Obviously, in all of oxychlorination reaction or direct catalytic oxidation of hydrogen chloride to chlorine, the regeneration of oxychlorination catalyst is the key step in order to fulfill the recycle of chlorine element. Lamberti et al. reported the experimental evidences of oxidation of CuCl to oxychloride Cu_2OCl_2 and neutralization of oxychloride to $CuCl_2$ in the ethylene oxychlorination (Eq. (5)) catalyzed by alumina-supported copper chloride at 500 K [36]. Ethylene oxychlorination follows a three-step mechanism: reduction of $CuCl_2$ by ethylene to CuCl; oxidation of CuCl by oxygen to oxychloride Cu_2OCl_2; rechlorination of oxychloride by HCl to $CuCl_2$.

$$C_2H_4 + 1/2O_2 + 2HCl \rightarrow C_2H_4Cl + H_2O \tag{5}$$

Opposite to the oxychlorination reaction of ethylene to 1,2-dichloroethane that has been widely investigated in the last decades [37–39], very few literature appeared for this analogous oxychlorination reaction of CO to phosgene although which is extremely industrially important. The direct experimental evidences of catalytic mechanism are still lacking so far and therefore seriously prevented us from deeply understanding and further effectively improving oxychlorination of CO to phosgene.

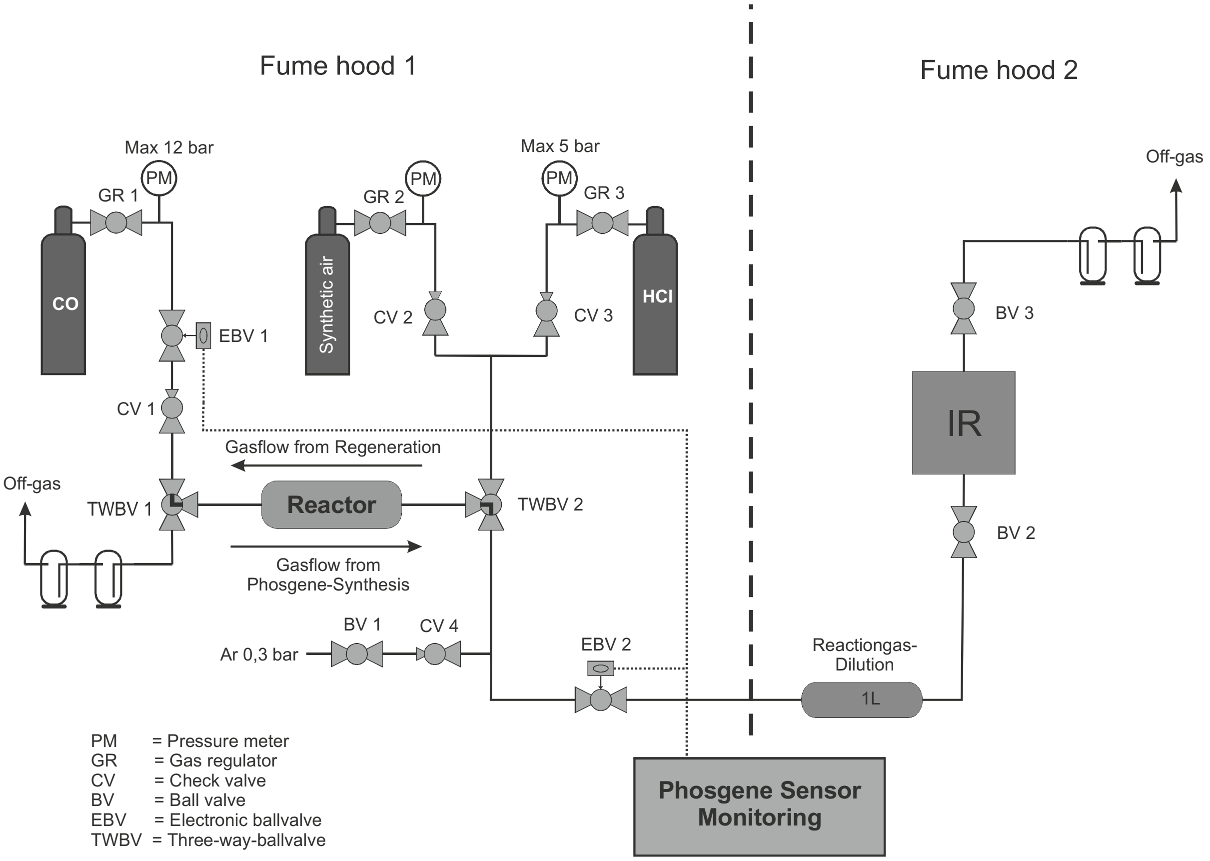
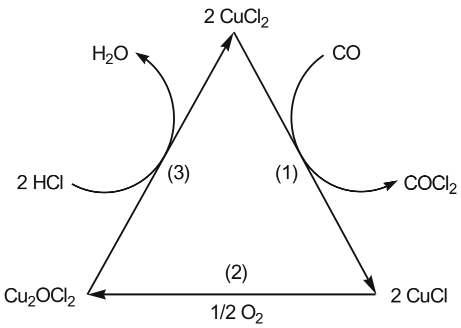


Fig. 1. The schematic view of the experiment set-up for oxychlorination of CO and regeneration of catalyst.

In our recent work, the kinetics of oxychlorination of carbon monoxide was investigated, and composition of catalyst was optimized systematically [40,41]. Here, we reported for the first time an effectively improved procedure, three-step reaction procedure, for the continuous preparation of phosgene from CO, air and HCl catalyzed by copper chloride and probed the corresponding catalytic mechanism of each step with XRD analysis. The regeneration conditions in the three-step reaction cycle were optimized.



Scheme 1. Schematic flow chart of three-step reaction cycle procedure.

The comparison of two-step and one-step regenerations indicates that the two-step regeneration process has some remarkable advantages in oxychlorination of CO to phosgene. Therefore, on the one hand, this three-step procedure offers a quite promising potential for the industrial use; on the other hand, the preliminary disclosure of catalytic mechanism will strongly promote further our understanding of oxychlorination of CO to phosgene catalyzed by $CuCl_2$ and contribute to make an improvement to this reaction.

2. Experiment

2.1. Apparatus

A special Cr–Fe alloy autoclave of 45 cm^3 (6.4 cm (length) × 3.0 cm (diameter)) was charged with 0.3361 g catalyst (containing 0.5 mmol $CuCl_2$) enclosed by an electrically heated tape. The product effluent was first diluted with 1 L Ar (0.25 bar) then was released to a Cyclone™ Gas cell (with base pathlength 12.5 cm,

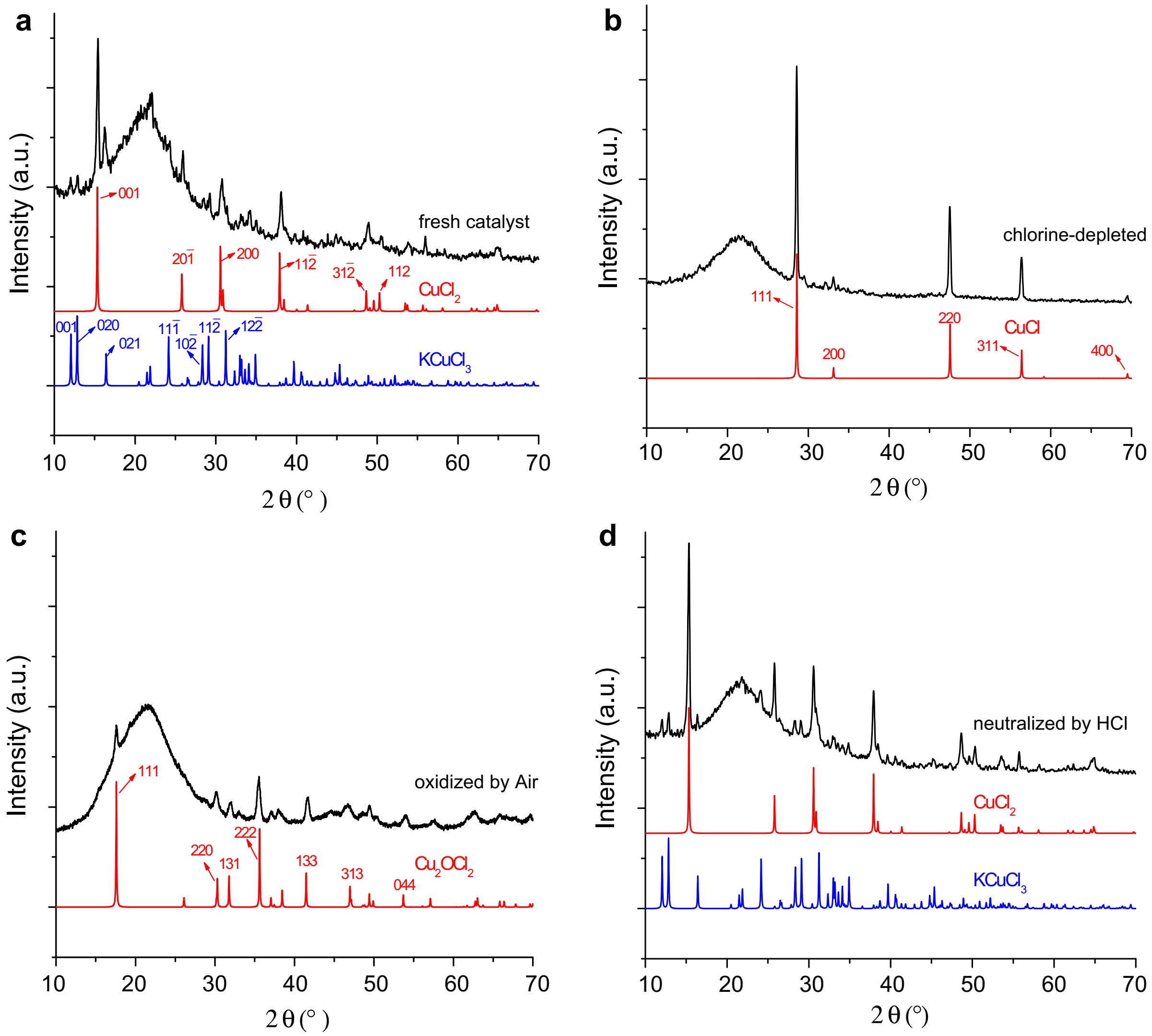


Fig. 2. Comparison of measured XRD patterns of the different kinds of copper species and calculated XRD patterns for crystallites $CuCl_2$, $KCuCl_3$, CuCl and Cu_2OCl_2: (a) the fresh catalyst, $CuCl_2$ and $KCuCl_3$; (b) the chlorine-depleted catalyst and CuCl; (c) the air-oxidized chlorine-depleted catalyst and Cu_2OCl_2; (d) the HCl-neutralized chlorine-depleted catalyst, $CuCl_2$ and $KCuCl_3$.

volume 0.19 L) installed on a Perkin Elmer Spectrum100 Series spectrometer to analyze the components of the product effluent online. The reactor off-gas was finally destroyed by a 25% aqueous solution of sodium hydroxide. The schematic experimental set-up is illustrated in Fig. 1.

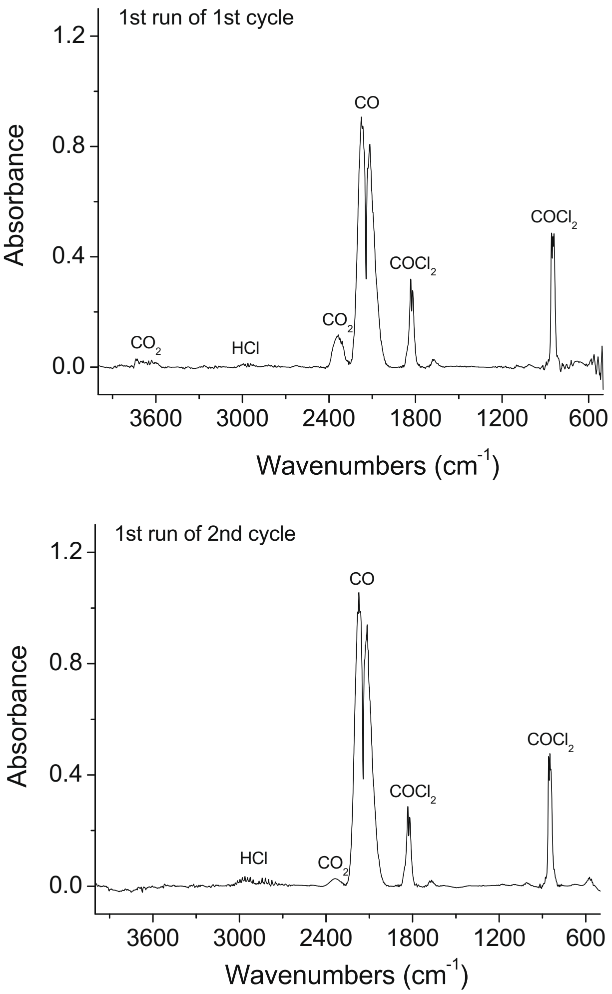


Fig. 3. Comparison of IR absorbance of the two-step regenerated catalyst and the fresh catalyst.

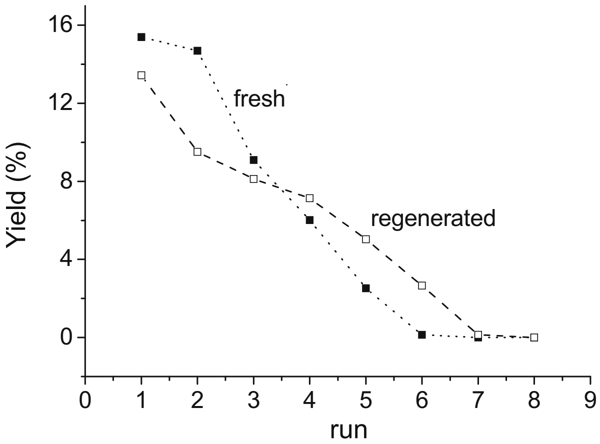


Fig. 4. Comparison of run curves of the two-step regenerated catalyst and the fresh catalyst.

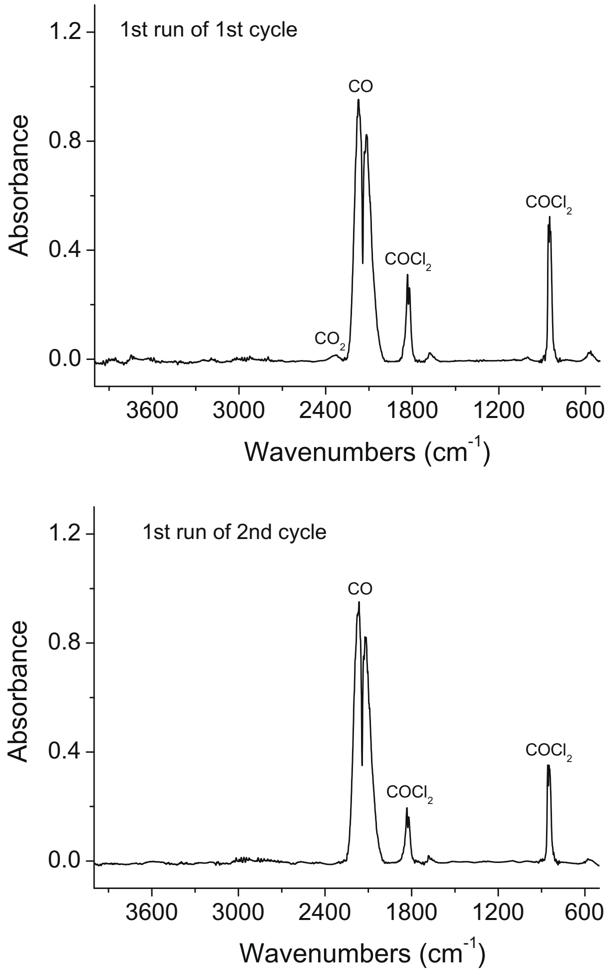


Fig. 5. Comparison of IR absorbance of the one-step regenerated catalyst and the fresh catalyst.

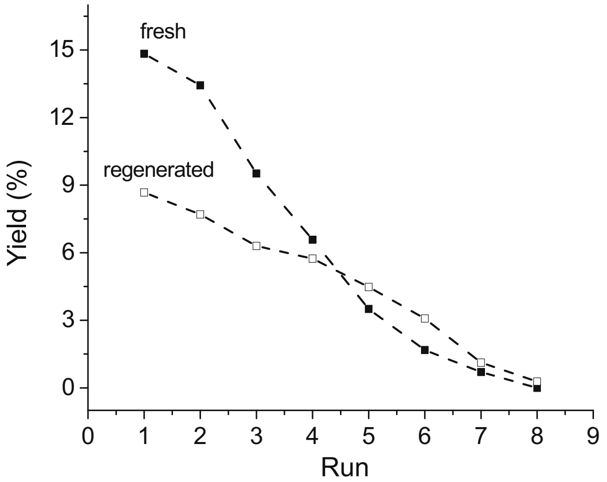


Fig. 6. Comparison of run curves of the one-step regenerated catalyst and the fresh catalyst.

2.2. Catalyst preparation

The catalysts were prepared by the incipient-wetness technique. 2.1524 g (16.0 mmol) $CuCl_2$ (Acros, 99%) and 0.2404 g (3.2 mmol) KCl (Merck, 99%) were dissolved in a minimum quantity of distilled water and then added to 8.3650 g silica gel (Grace, surface area 25 $m^2\,g^{-1}$, pore volume 0.9 mL g^{-1}). The obtained paste was first rotary evaporated then dried at 120 °C in an oven for 2 h. The composition of the prepared catalyst is 20 wt.% $CuCl_2$, molar ratio of $CuCl_2$:KCl is 5:1, which is denoted as 20Cu:4K/SiO_2.

2.3. EDX and SEM measurements

The energy-dispersive X-ray (EDX) and scanning electron microscopy (SEM) experiments were conducted on a Hitachi TM-1000 instrument operated at 200 kV or on EDAX instrument from

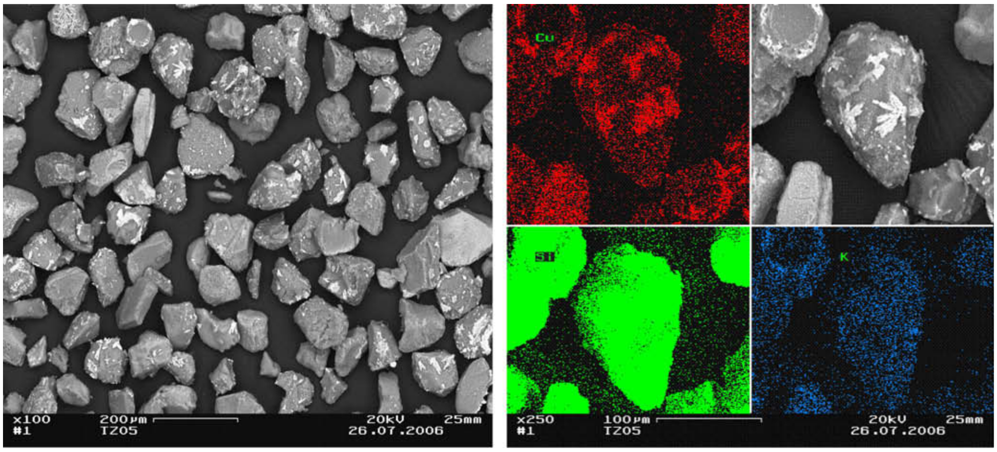


Fig. 7. The morphologies of the fresh catalyst (left: SEM, right: EDX).

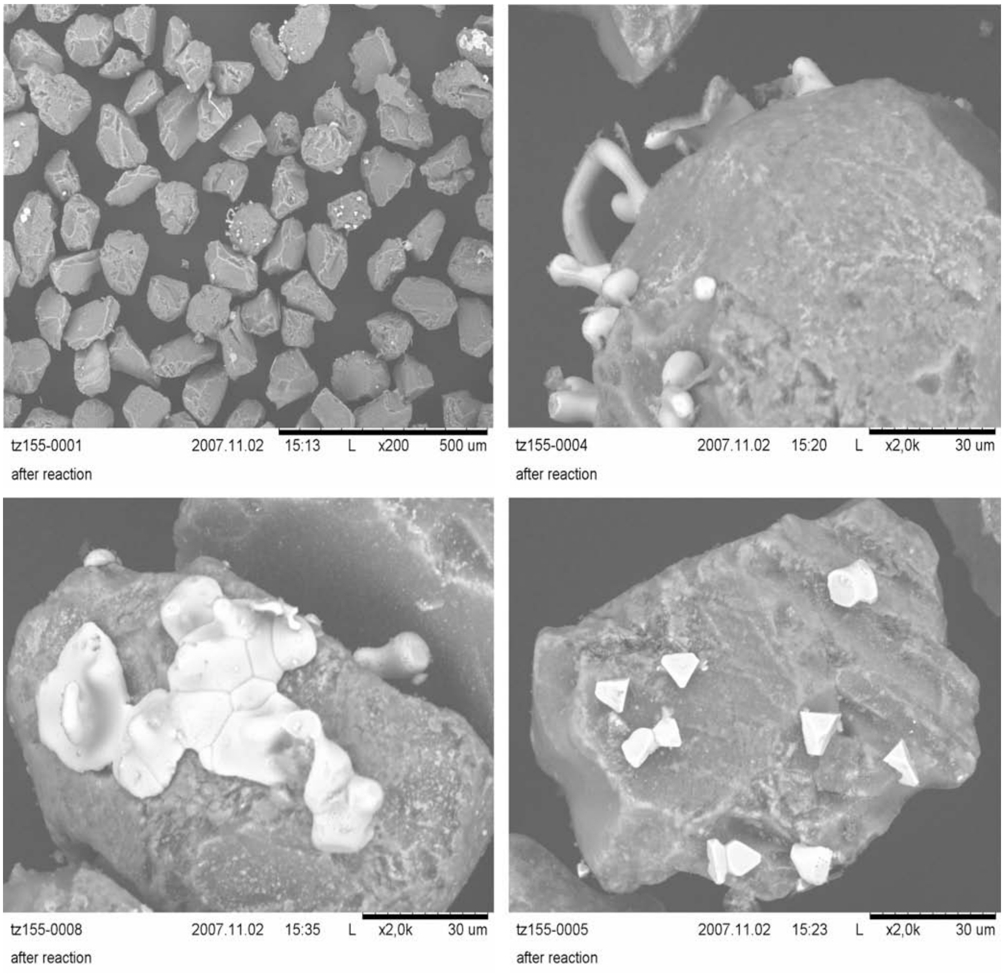


Fig. 8. The morphologies of the chlorine-depleted catalyst (300 °C, 5 bar CO, 6 min).

EDAX Inc. According to the principle of EDX, heavy atoms, like Cu and K, have a stronger ability to reflect the X-ray than light atoms Si, O, C and Cl. Therefore, in SEM pictures, the bright area indicates the dispersion of metal atoms. According to the shape and size of the bright area of silica surface, the dispersion information of $CuCl_2$/KCl can be obtained.

2.4. X-ray powder diffraction

The copper species of catalyst in the different stages were identified on a STOE STADI powder diffractometer equipped with a linear position sensitive detector, using Cu-Kα radiation ($\lambda = 1.5406$ Å, $10^\circ \leqslant 2\theta \leqslant 100^\circ$, step width = 0.01°) in transmission mode. Microcrystalline diamond was used as the internal standard. The patterns were indexed by using the software package WinXPOW (Stoe) and refined with the WinPLOTR program [42]. The crystalline structure of the present phases was identified through comparison with the powder XRD patterns calculated from crystal structure data of the American Mineralogist Crystal Structure Database (AMCSD) [43].

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

To the autoclave charged with 0.3361 g fresh catalyst (20 Cu:4 K/SiO_2) (including 0.5 mmol $CuCl_2$) at 300 °C, 5 bar CO (4.7 mmol) was fed. The reaction time is 6 min. Following the earlier mentioned reaction conditions, the catalyst was continuously run several times until all active $CuCl_2$ is depleted. The concentration of phosgene in the product effluent was calculated according to the IR absorption area (at 1827 cm^{-1}) following the Eq. (6) [40]:

$$A = 1 + 42.3X \tag{6}$$

where A is the absorption area (at 1827 cm^{-1}) of phosgene, and X is molar percentage of phosgene (mol%) in the product effluent. The yield of phosgene was calculated based on the amount of copper chloride (0.5 mmol) because CO was fed to excess (4.7 mmol) (Eq. (7)). The yield of each run is added together to obtain the cumulative yield (cy), which indicates the effectively utilized amount of $CuCl_2$ in the catalyst. The yield of the first run is considered as the single-run yield (sy).

2.6. Regeneration of catalyst with the two-step or one-step procedure

After the catalyst was exhausted, the regeneration reaction was immediately performed following a two-step or one-step procedure:

Two-step regeneration procedure: First, air (pressure 1–5 bar) was fed to the autoclave at 300 °C and kept t_o min. After the oxidation of t_o min, air was released, and then the autoclave was flushed with Ar. Then, dry HCl (pressure 1–3 bar) gas was fed and kept t_n min. After the neutralization of t_n min, unreacted HCl was released to an aqueous solution of sodium hydroxide. The total regeneration time is sum of oxidation time and neutralization time, $t_o + t_n$ min.

(1) Oxidation step (Eq. (8)): temperature 300 °C, air 1–5 bar, time t_o min
(2) Neutralization step (Eq. (9)): temperature 300 °C, HCl 1–3 bar, time t_n min

One-step regeneration procedure (Eq. (4)): First, 3.0 bar HCl was fed to the autoclave, and then immediately 5.0 bar air was fed.

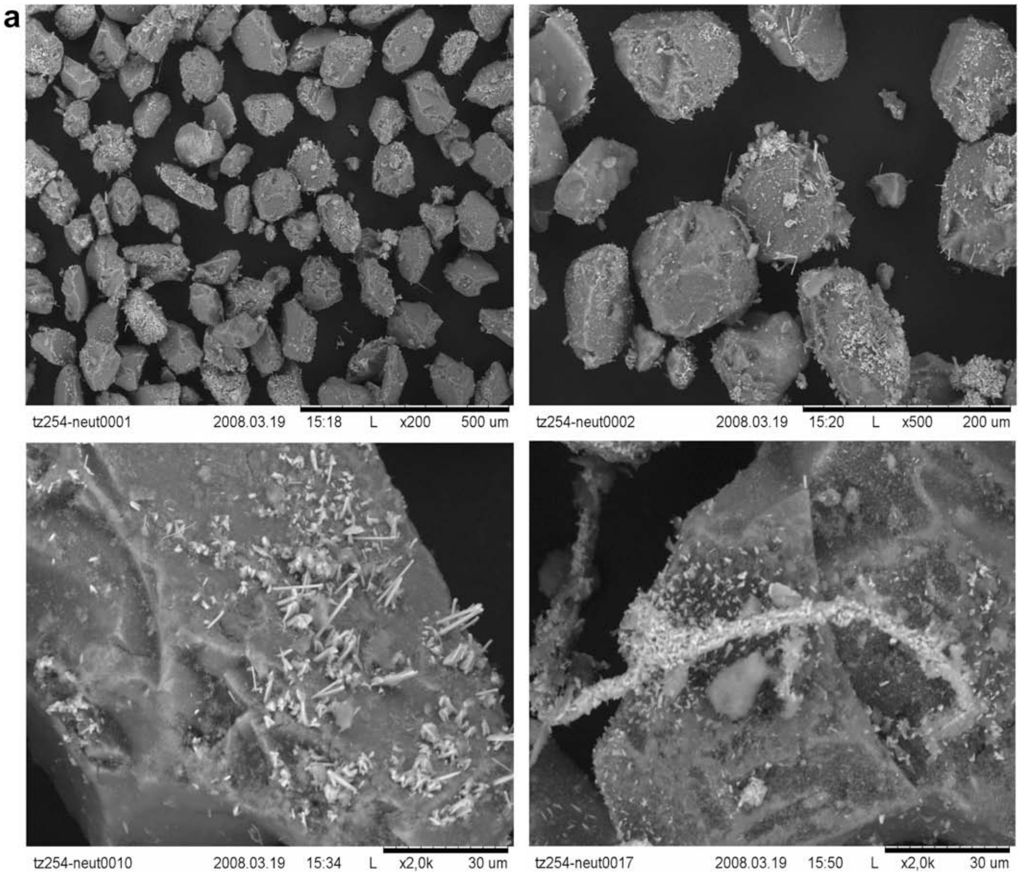


Fig. 9. The morphologies of the two-step regenerated catalyst. (a) 300 °C, 5 bar air, 6 min and (b) 300 °C, 3 bar HCl, 6 min.

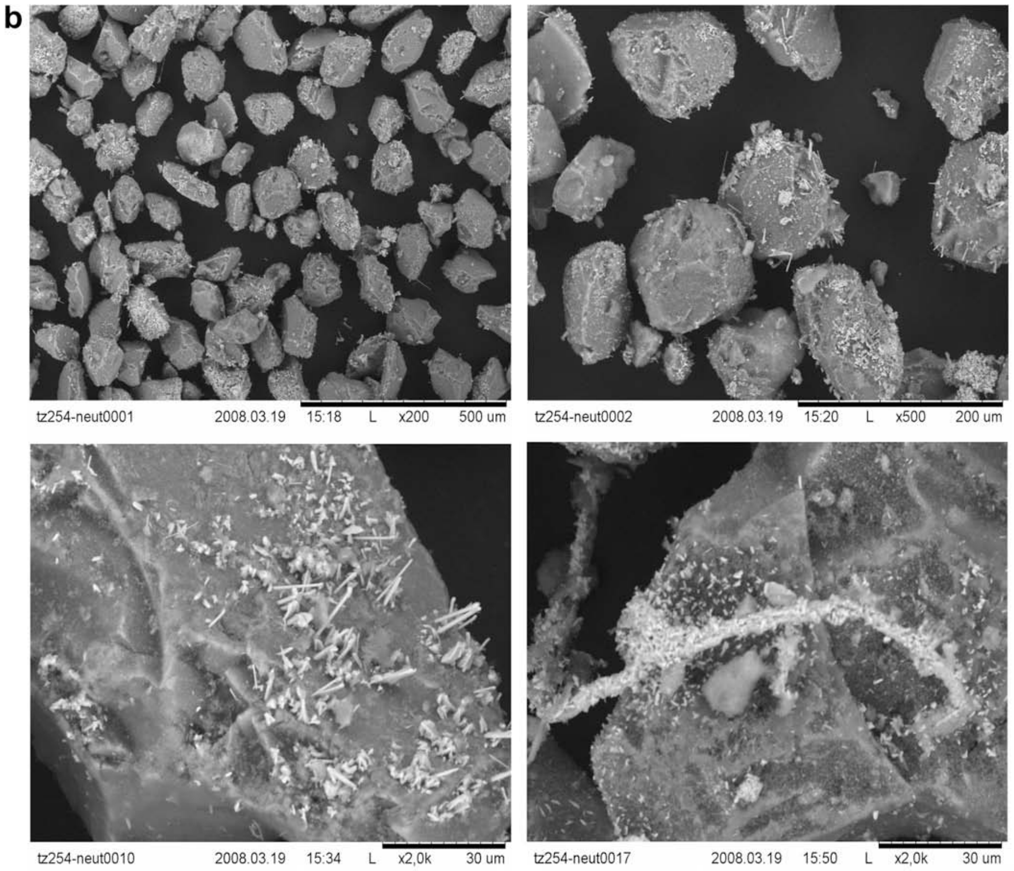


Fig. 9 (*continued*)

The pressure in the autoclave is finally 8.0 bar. After 6 min regeneration, unreacted air and HCl were released to the aqueous solution of sodium hydroxide. This one-step regeneration was carried out as a control experiment of the two-step regeneration.

3. Results and discussion

The oxychlorination of CO to phosgene in a three-step reaction cycle was illustrated in Scheme 1.

In Scheme 1, there are three separate steps: the first step is the oxychlorination of CO to phosgene and simultaneous reduction of $CuCl_2$ to CuCl (Eq. (7)); the second one is the oxidation of CuCl with air to Cu_2OCl_2 (Eq. (8)), and the third one is the neutralization of Cu_2OCl_2 with HCl to $CuCl_2$ (Eq. (9)). The regeneration of chlorine-depleted catalyst consists of steps 2 and 3, which is called the two-step regeneration procedure. In the earlier reaction cycle, the masses containing copper chloride cannot be qualified as catalyst. For convenience, we still call the mass as "catalyst".

$$2CuCl_2 + CO = COCl_2 + 2CuCl \tag{7}$$

$$2CuCl + 1/2O_2 = Cu_2OCl_2 \tag{8}$$

$$Cu_2OCl_2 + 2HCl = 2CuCl_2 + H_2O \tag{9}$$

The earlier proposed mechanism of each step in Scheme 1 was preliminarily confirmed by XRD measurements (Fig. 2).

Fig. 2 shows the comparison of the measured XRD patterns of copper species in the different stages and the calculated XRD patterns for crystallites $CuCl_2$, $KCuCl_3$, CuCl and Cu_2OCl_2.

In Fig. 2a, two phases were found: one is from $CuCl_2$, and another is from $KCuCl_3$ in the fresh catalyst. In order to improve the activity of $CuCl_2$, the promoter KCl was added, therefore, double salt $KCuCl_3$ was formed [44,45]. The peaks at $2\theta = 15.4°$, 26.0°, 30.8°, 38.1°, 48.9° and 50.5° may be assigned to the reflection of planes of (0 0 1), (2 0 −1), (2 0 0), (1 1 −2), (3 1 −2) and (1 1 2) in crystallite $CuCl_2$ (space group *C*2/m), respectively [46]. The peaks at $2\theta = 12.1°$, 12.8°, 16.4°, 24.2°, 28.4°, 29.1° and 31.2° may be assigned to the reflection of planes of (0 0 1), (0 2 0), (0 2 1), (1 1 −1), (1 0 −2), (1 1 −2) and (1 2 −2) in crystallite $KCuCl_3$ (space group $P2_1/c$), respectively [47].

In Fig. 2b, the chlorine-depleted catalyst mainly includes CuCl, and double salt $KCuCl_3$ disappeared. The peaks at $2\theta = 28.6°$, 33.1°, 47.5°, 56.4° and 69.5° may be assigned to the reflection of planes of (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (4 0 0) in crystallite CuCl (space group *F*-43 m (2 1 6)), respectively [48].

In Fig. 2c, CuCl was oxidized to Cu_2OCl_2 by air. The peaks at $2\theta = 17.6°$, 30.2°, 32.0°, 35.5°, 41.7°, 46.7° and 53.9° may be assigned to the reflection of planes of (1 1 1), (2 2 0), (1 3 1), (2 2 2), (1 3 3), (3 1 3) and (0 4 4) in crystallite Cu_2OCl_2 (space group *F*ddd (7 0)), respectively [49].

In Fig. 2d, Cu_2OCl_2 was neutralized to $CuCl_2$ by HCl, and $KCuCl_3$ was formed again; The XRD patterns were recovered to the original one similar to patterns shown in Fig. 2a.

Although the relative intensity of peaks is difficult to calculate accurately due to the strong background from the amorphous silica gel, on the whole, the measured XRD patterns are in excellent agreement with the calculated patterns for crystallites $CuCl_2$, $KCuCl_3$, CuCl and Cu_2OCl_2. It is very necessary to point out here that the earlier XRD measurements were not carried out under reaction conditions online due to the limited experimental set-up, therefore, potential hydration/restructuring of substance possibly occurred. In order to avoid hydration/restructuring and obtain a real-time state as well as non-crystalline phases of materials, the combined

XRD/XAFS methods will be employed in the further investigation. Therefore, the proposed mechanism of each step in three-step reaction cycle was proved preliminarily by XRD analysis here.

3.1. Two-step regeneration procedure versus one-step regeneration procedure

3.1.1. The degree of recovery of the catalyst

After the regeneration, the degree of recovery of the catalyst from the two-step and one-step procedure was compared. Here, two-step regeneration conditions are (1) 300 °C, 5 bar air, 6 min; (2) 300 °C, 3 bar HCl, 6 min.

Degree of recovery was calculated as follows:

Degree of recovery for the single-run yield (sy): $\frac{sy_r}{sy_f} \times 100\%$
Degree of recovery for the cumulative yield (cy): $\frac{cy_r}{cy_f} \times 100\%$
sy_f and cy_f: the single-run yield and the cumulative yield for the fresh catalyst;
sy_r and cy_r: the single-run yield and cumulative yield for the regenerated catalyst.

3.2. The degree of recovery of the single-run yield or cumulative yield from two- or one-step regeneration

The Fig. 3 shows the IR spectra comparison of results from the fresh catalyst and two-step regenerated catalyst. For the result from two-step regeneration, the degree of recovery for the single-run yield is 87.0%. The two run curves of the fresh catalyst and regenerated catalyst almost overlap completely. The degree of recovery for the cumulative yield is 97.0% (Fig. 4).

However, for the result from the one-step regeneration procedure, the degree of recovery for the single-run yield is only 58.8% (Fig. 5), the degree of recovery for the cumulative yield is about 80.5% (Fig. 6).

The reasons why the degree of recovery for the single-run yield or the cumulative yield in the three-step procedure is remarkably higher than that in the one-step regeneration procedure can be summarized as follows.

Based on the analysis of the thermodynamical data and the mechanism of the reaction, two main drawbacks can be overcome effectively using this three-step procedure, and therefore, the degree of recovery of catalyst was greatly improved.

3.2.1. Prevention of the disproportionation of Cu (I)

In the one-step regeneration, oxidation and neutralization almost simultaneously proceed, the formed water will contribute to the disproportionation of Cu (I) to Cu (II) and Cu (0) (Eq. (10)). According to the redox potentials, the equilibrium constant is $K = 1.3 \times 10^6$ at 298 K. So the reaction is highly favorable [50]. Under this regeneration conditions, the oxidation of Cu (0) to Cu (II) will not take place easily because the oxide film was formed and the reaction time is too short.

$$2\text{Cu}^{2}(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s}) \quad \Delta_r H_m^{\circ} = -42.1\ \text{kJ/mol} \tag{10}$$

However, when the oxidation and neutralization is carried out in two separate steps, the disturbance of water can be prevented effectively. In the oxidation step, according to the thermodynami-

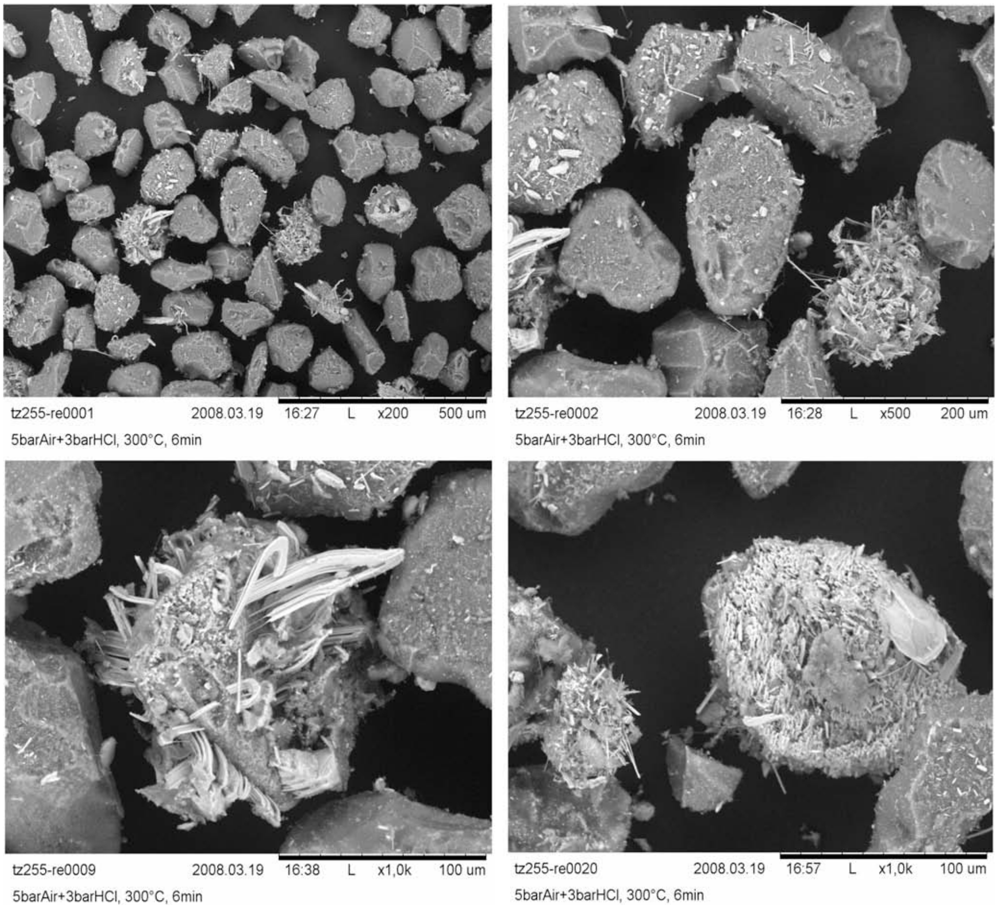


Fig. 10. The morphologies of the one-step regenerated catalyst.

cal calculation, the disproportionation of Cu (I) at the absence of water is very difficult (Eq. (11)). It is an endothermal reaction with an enthalpy $\Delta_r H_m^0$ of 872.1 kJ mol^{-1}. This should lead to a more defined reaction pathway where Cu (I) is completely oxidized to Cu (II) and then converted to $CuCl_2$ in the neutralization.

$$2Cu^{+}(g) \rightarrow Cu^{2+}(g) + Cu(s) \quad \Delta_r H_m^{\circ} = 872.1\ \text{kJ/mol} \qquad (11)$$

3.2.2. Prevention of the undesirable Deacon reaction

Another problem for the one-step regeneration is that in a Deacon reaction chlorine can be produced at 650–750 K. In the presence of $CuCl_2$, HCl can be oxidized to Cl_2 with oxygen, which also decreases the efficiency of the regeneration to some extent [51]. In the two-step regeneration procedure, air and HCl cannot meet in the reactor; therefore, the Deacon reaction here can be suppressed.

3.3. The influence of the regeneration on the morphologies of catalyst

The dispersion of $CuCl_2$/KCl on the surface of silica in the fresh catalyst is not homogeneous due to the interface tension [52], namely, the silica surface cannot be uniformly covered by Cu–chloride species. Some lumps of $CuCl_2$/KCl crystal were accumulated on the surface of silica (Fig. 7). During the reaction, $CuCl_2$/CuCl/KCl is in a molten state. After the reaction was finished and cooled to r.t., CuCl/KCl solidified in the different shapes (Fig. 8). However, after the oxidation, these CuCl/KCl forms were broken into smaller pieces (Fig. 9a). The further neutralization leads to numerous short needle-like crystals on the surface of silica (Fig. 9b). Therefore, after the two-step regeneration, the dispersion of $CuCl_2$/KCl on silica was slightly improved. For the one-step regeneration, a lot of thicker and curly extrudates were formed that probably result from extrusion through silica pores (Fig. 10).

3.4. The influence of regeneration time (t_o:t_n = 1:1) on the degree of recovery

In this experiment, the ratio of oxidation t_o to neutralization t_n was kept 1:1, the total regeneration time t (=$t_o + t_n$) increase from 1 min to 20 min with a interval of 2 min. Fig. 11 shows the influence of regeneration time on the degree of recovery of the single-run yield or cumulative yield. When the regeneration time is very short, say, 1 min, the degree of recovery for the single-run yield and cumulative yield is only 74.7% and 77.5%, respectively. When the regeneration was increased to 4–16 min, the degree of recovery of the cumulative yield is about 96.0%. If the regeneration time is too long, say, 20 min, the recovery is inversely decreased. While the recovery of the single-run yield always fluctuates around about 75.0% with the regeneration time. Therefore, the regeneration time of 2–6 min is better.

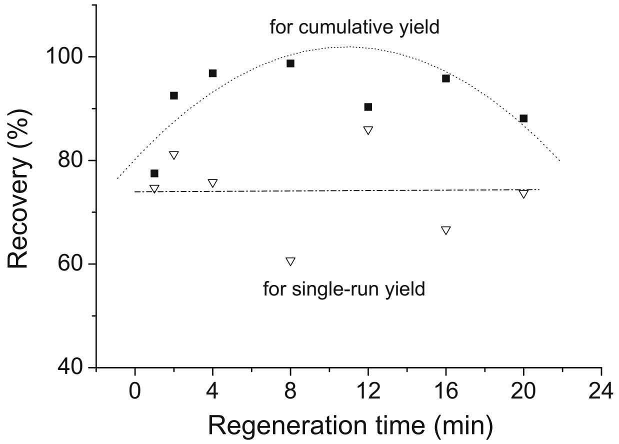


Fig. 11. The influence of CO pressure on the yield of phosgene with the reaction time of 10 min at 345 °C.

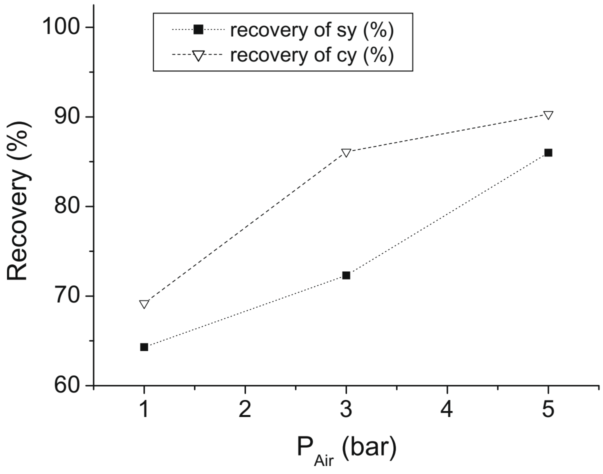


Fig. 12. The influence of pressure of air on the degree of recovery (pressure of HCl is 3 bar).

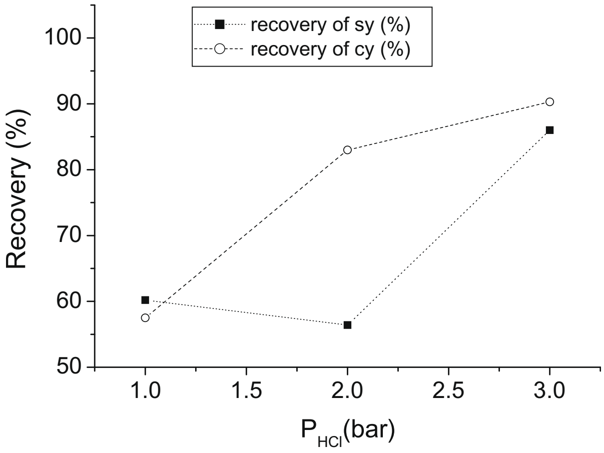


Fig. 13. The influence of pressure of HCl on the degree of recovery (pressure of air is 5 bar).

3.5. The influence of pressure of air or HCl on the degree of recovery

In order to fully convert Cu (I) chloride to Cu (II) chloride, the excess of air and HCl is necessary. The recovery of the single-run yield and cumulative yield approximately increases linearly with the pressure of air (pressure of HCl was 5 bar) (Fig. 12). The similar case can be found when the pressure of HCl increases from 1 bar to 3 bar (pressure of air was 5 bar) (Fig. 13). The reason is understandable. Since the dispersion of $CuCl_2$/KCl is heterogeneous, with the increasing pressure of either air or HCl, air or HCl can penetrate inside the crystal of $CuCl_2$/KCl, therefore more complete oxidation and neutralization can occur.

4. Conclusions

In this work, for the first time, a three-step reaction procedure was proposed to produce continuously phosgene from HCl, air and CO catalyzed by $CuCl_2$ where the regeneration of catalyst consists of the oxidation and neutralization. The two-step regeneration conditions were optimized. Compared with the one-step regeneration procedure, the two-step regeneration can effectively prevent the disproportionation of Cu (I) and a type of Deacon reaction. At the same time, the dispersion of $CuCl_2$/KCl on the silica surface from the two-step regeneration is better than that from one-step regeneration. Finally, the degree of recovery of the single-run yield and cumulative yield for the two-step regeneration can reach up to 87.0% and 97.0%, respectively when the regeneration conditions are 5 bar air (6 min) and 3 bar HCl (6 min) at 300 °C. Therefore, this three-step reaction cycle provides a potential approach to the industrial production of phosgene. Furthermore, the preliminary disclosure of reaction mechanism by XRD measurements can help us effectively to deepen the understanding of this important oxychlorination of carbon monoxide to phosgene. Without doubt, these results are quite interesting for both industrial field and academic research.

Acknowledgments

The authors thank the financial support from Bayer Material Science AG and T. Zhang thanks Dr. Peter Reuter and Dr. Christian Hanisch for EDX measurements at Universität Ulm, Dr. Florian Kraus and Dr. Bernhard Wahl for XRD measurements, Dr. Tobias Förstern for CO adsorption experiment at TU München.

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