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Converting industrial waste contact masses into effective multicomponent copper-based catalysts for the Rochow process

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ABSTRACT

In this work, we report a simple and inexpensive approach to synthesize effective multicomponent Cu–Cu_2O–CuO catalysts for the Rochow process from industrial waste contact masses (WCMs). WCMs from the organosilane industry were treated with acid followed by reduction with metallic iron powder. The obtained copper powder was then subjected to controlled oxidation in air at different temperatures, followed by ball milling. The orthogonal array approach was applied to optimize this process, and the stirring speed and pH were found to significantly affect the leaching ratio and copper yield, respectively. When used for the Rochow process, the optimized ternary Cu–Cu_2O–CuO catalyst greatly enhanced the dimethyldichlorosilane selectivity and Si conversion compared with Cu–Cu_2O–CuO catalysts prepared without ball milling, bare Cu catalysts, and Cu–Cu_2O–CuO catalysts with different compositions. This could be attributed to their small particle size and the strong synergistic effect among the multiple components in the catalyst with the optimized composition.

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Introduction

The Rochow process was discovered in the 1940s and is still the most economical way to produce monomers for silicone synthesis in the organosilane industry (Hurd & Rochow, 1945). In this reaction, gaseous methyl chloride (MeCl) reacts with metallurgical grade silicon (Si) powder with the assistance of copper (Cu)-based catalysts and some promoters as follows:

$$\mathrm{Si}+\mathrm{CH_3Cl}\underset{300-350^{\circ}\mathrm{C}}{\overset{\text{Cu catalyst}}{\rightarrow}}\begin{cases}(\mathrm{CH_3})_3\mathrm{SiCl}\\(\mathrm{CH_3})_2\mathrm{SiCl_2}\\\mathrm{CH_3SiCl_3}\\\mathrm{CH_3HSiCl_2}\\\mathrm{CH_3H_2SiCl}\\\text{Volatiles with low boiling points}\\\text{Volatiles with high boiling points}\end{cases}. \qquad (1)$$

This process gives various methylchlorosilane products. Among them, dimethyldichlorosilane ($(CH_3)_2SiCl_2$, M2) is the most desirable because it serves as the primary monomer for the preparation of silicone products in the organosilane industry (Ehrich, Born, Richter, Richter-Mendau, & Lieske, 1997; Gordon, Hinch, & Strongin, 2009; Lieske & Zimmermann, 1995; Ward, Ritzer, Carroll, & Flock, 1986). To improve the M2 yield, many studies have investigated highly efficient catalyst systems (Bablin, Crawford, DeMoulpied, & Lewis, 2003; Bablin, Lewis, Bui, & Gardner, 2003; Floquet, Yilmaz, & Falconer, 1994; Gasper-Galvin, Sevenich, Friedrich, & Rethwisch, 1991; Hashiguchi, Dietrich, & Schoepe, 1985; Kim & Rethwisch, 1992; Lewis, Ligon, & Carnahan, 2002; Lewis & Ward, 2002; Sun, Bent, Wright, & Naasz, 1998; Zhu et al., 2013). Among these systems, the ternary Cu-based catalysts containing Cu, Cu_2O, and CuO are of particular interest because of their excellent catalytic performances (Ehrich et al., 1997; Hashiguchi et al., 1985; Lieske & Zimmermann, 1995; Ward et al., 1986). However, because of limitations from reaction kinetics and reactors, the Rochow process inevitably generates waste contact masses (WCMs), which contain 5%–25% of Cu compounds and 75%–95% of Si by mass. With rapid growth in the production capacity of organic silicon monomers, a continuous increase in the formation of WCMs has occurred in recent years. These solid wastes

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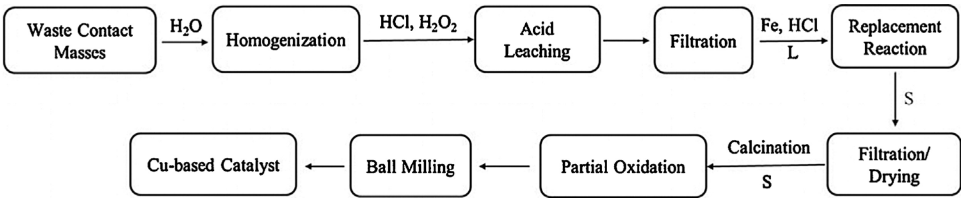

Fig 1. The process for preparation of the Cu-based catalyst.

are commonly buried, which often causes serious environmental pollution and is a waste of resources. For sustainability reasons, these WCMs should be recycled. Previously, we demonstrated that Si powder in WCMs could be re-used for fabrication of high capacity anodes for Li-ion batteries (Yu et al., 2013; Zhang et al., 2014). However, to date, few studies have reported on the recovery of valuable metals from WCMs and the further exploration of their potential applications.

Considering that multicomponent Cu–Cu_2O–CuO catalysts are in great demand in the Rochow process, we developed a simple and effective approach to recover copper from WCMs for the preparation of an effective multicomponent Cu–Cu_2O–CuO catalyst. In this process, WCMs were subjected to acid leaching treatment and the resulting Cu^{2+} ions were then reduced to Cu powder by metallic iron (Fe) powder. This was followed by controlled oxidation in air at various temperatures and ball milling. The obtained multicomponent Cu–Cu_2O–CuO catalysts exhibited much higher M2 selectivity and Si conversion in the Rochow process compared with sole Cu catalysts, Cu–Cu_2O–CuO catalysts prepared without ball milling, and Cu–Cu_2O–CuO catalysts with different compositions. Therefore, small particles and the synergistic catalytic effect among the multiple components are important in determining the catalytic effect. The obtained multicomponent Cu–Cu_2O–CuO catalysts were re-used in the Rochow synthesis to examine the catalytic properties.

Experimental

Sample preparation

The preparation process of the Cu-based catalyst is illustrated in Fig. 1. The first stage was acid leachin. First, 1000 g of WCMs (Jiangsu Hongda New Material Co., Ltd., Yangzhong, China) was dispersed in 1000 mL of deionized water under stirring to form a homogeneous suspension. Then, 50–200 mL of hydrogen peroxide (H_2O_2, 30 wt%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and 200–400 mL of hydrochloric acid (HCl, 36.5 wt%, Sinopharm Chemical Reagent Co., Ltd.) were added successively, followed by stirring (0–600 rpm) for 2 h. Finally, the resulting mixture was filtered to obtain the leachate.

The second stage was replacement of Cu. A given amount of Fe powder as a reducing agent was added to the above leachate, then HCl was introduced to adjust the solution pH to between 1.0 and 4.0. After 4 h at a set temperature between 20 and 80 °C, the solution was filtered to remove the liquid waste, and excess Fe was removed by dissolving it in a dilute HCl solution. The obtained solid was dried under vacuum at 80 °C for 8 h. The sample prepared in this manner was named R-Cu.

The leaching ratio of copper was calculated by Eq. (2) as follows:

$$\text{Leaching ratio}(\%) = \frac{W1}{W2} \times 100\%, \tag{2}$$

where W1 represents the actual mass (g) of R-Cu and W2 represents the theoretical mass (g) of Cu in the WCM.

The copper yield was calculated using Eq. (3) as follows:

$$\text{Copper yield}(\%) = \frac{C1 - C2}{C1} \times 100\%, \tag{3}$$

where C1 represents the concentration (mol/L) of Cu^{2+} ions before the reaction and C2 represents the concentration (mol/L) of Cu^{2+} ions after the reaction.

The last stage was partial oxidation, followed by ball milling. Typically, 10.0 g of R-Cu was placed in a square crucible, which was then put in a muffle furnace. The samples were oxidized in air at 50, 100, or 200 °C for 1 h, labeled as S1, S2, and S3, respectively. After ball milling for 2 h at 580 rpm, Cu-based catalysts containing Cu, Cu_2O, and CuO were obtained and labeled as S1-M, S2-M, and S3-M, respectively.

Characterization

X-ray diffraction (XRD) patterns were recorded on a X'Pert PRO MPD (PANalytical, Netherlands) using Cu Kα radiation (λ = 1.5418 Å). The crystallite size was calculated using the Scherrer equation, in which the shape factor K is 0.90. The 2θ value of instrumental broadening was 0.06, and this was subtracted in the test process. The morphologies and sizes of the samples were observed by field-emission scanning electron microscopy (SEM) (JSM-7001F, JEOL, Tokyo, Japan) with energy-dispersive spectroscopy (INCA X-MAX, JEOL). Thermal gravimetric (TG) analysis was carried out with an EXSTAR TG/DTA 6300 (Seiko Instruments, Japan) instrument. H_2-temperature programmed reduction profiles were recorded on an automated chemisorption analyzer (ChemBET pulsar TPR/TPD, Quantachrome, USA). Typically, 0.1 g of sample was loaded into a quartz U-tube and degassed in He at 150 °C for 30 min. After the temperature was dropped to 30 °C, the gas was changed to 9.9% H_2 in He (30 mL/min). Finally, the sample was heated at a rate of 10 °C/min from 30 to 900 °C. The particle size distribution was measured using a laser particle size analyzer (BT-9300Z, Bettersize Instruments Ltd., China). The composition of R-Cu was quantified by inductively coupled plasma optical emission spectrometry (Optima 5300DV, Perkin Elmer, USA) after dissolving the samples in a HNO_3 solution.

A redox titration was used to measure the contents of Cu, Cu_2O, and CuO in the samples. Typically, 0.3 g of sample was placed in a flask containing 120.0 mL of acetonitrile (CH_3CN, 95%), followed by the addition of 40.0 mL of dilute HCl (18.5 wt%). After vigorous shaking for 20 s, the mixture was filtered immediately. Subsequently, 160.0 mL of deionized water was added to the filtrate, which was then titrated with 0.02 mol/L of an aqueous $KMnO_4$ solution ($\geq$99.5%) (Eq. (4)). The residual solid precipitate was dissolved in 20.0 mL of $FeCl_3$ solution (0.1 mol/L), kept at 50 °C in a water bath, and then cooled to room temperature (Eq. (5)). Afterwards, 20.0 mL of $MnSO_4$ solution (0.7 mol/L) and 100.0 mL of deionized water were introduced, and the sample was again titrated with 0.02 mol/L of $KMnO_4$ solution (Eq. (6)). The content of Cu_2O in the sample was calculated by the amount of $KMnO_4$ consumed in Eq. (4), and the content of Cu was calculated using the amount of Fe^{2+} derived from the amount of $KMnO_4$ consumed in Eq. (6). The con-

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