Chemical Engineering Journal 226 (2013) 161–165

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Low temperature hydrolysis of carbonyl sulfide using Zn–Al hydrotalcite-derived catalysts

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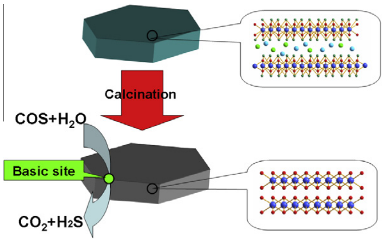
HIGHLIGHTS

- Zn–Al hydrotalcite-derived oxides have been prepared and characterized.
- Hydrolysis of COS over Zn–Ni/Al hydrotalcite-derived oxide was studied.
- Effect of calcination temperature and pH on catalysts was described.
- Effect of H_2O, and O_2 on hydrolysis process of COS was studied.

GRAPHICAL ABSTRACT

Catalytic hydrolysis of carbonyl sulfide (COS) at 50 °C over Zn–Al mixed oxides derived from hydrotalcite-like compounds was studied.



ARTICLE INFO

Article history:
Received 28 December 2012
Received in revised form 26 March 2013
Accepted 10 April 2013
Available online 19 April 2013

Keywords:
Carbonyl sulfide
Hydrolysis
Hydrotalcite-like compounds
Zn–Al catalyst

ABSTRACT

A series of Zn–Al hydrotalcite-like compounds (HTLCs) were synthesized by co-precipitation method. The mixed oxides derived from HTLCs were tested for the catalytic hydrolysis of carbonyl sulfide (COS) at relatively low temperatures of 50 °C. These catalysts were characterized by X-ray diffraction (XRD) and Thermogravimetry/Derivative Thermogravimetry Analysis (TG-DTA) and the results can help us to understand the effect of preparation conditions. The results showed that the Zn–Al hydrotalcite-like compounds were efficient precursor in preparing active and stable catalysts for hydrolysis of COS. The catalyst performance was strongly related to the synthesis pH and calcination temperature. The optimum condition was pH of 10, and calcination temperature of 400 °C. Although water was indispensable for hydrolysis of COS, the excess water would hinder the adsorption of COS. In general, COS was hydrolyzed to H_2S, which is depending on the chemistry of the derived oxides. The end-products of hydrolysis were simple substance S and sulfate. The presence of oxygen will accelerate the formation of the final product.

1. Introduction

Carbonyl sulfide (COS), widely exists in natural gas, petroleum gas, water gas and industrial tail gas, is normally regarded as a significant poison which can cause the deactivation of the industrial catalyst. Even only trace amount of COS can result in the deactivation of catalysts and lead to corrosion of reaction equipments [1–3]. For instance, sulfide in the form of COS will poison the catalyst in the Fischer–Tropsch process and sulfide content in the feed should be kept below 0.02 mg/m^3 [4]. Furthermore, not only does COS cause economic loss, but also affects the environment. It has been proven to be a major source of acid rain when oxidized to sulfur oxide and to promote photochemical reactions [5]. COS is difficult to be removed efficiently by the conventional method of desulphurization. Among the methods for COS removal, COS hydrolysis ($COS + H_2O = CO_2 + H_2S$) is recognized as the most promising method due to the mild reaction condition and higher removal efficiency [6,7]. Due to the limitations of industrial reaction conditions (low reaction temperature and low COS concentrations), development of an efficient catalyst for the low temperature hydrolysis is necessary. Up to now, a number of different types of COS hydrolysis catalysts have been investigated and most of them

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http://dx.doi.org/10.1016/j.cej.2013.04.039

are based on activated carbons [8,9] or metal oxides [10,11] with different promoters, such as alkali metal oxides, alkali earth metal oxides and/or transition metal oxides. West et al. [12] and Huang et al. [13] showed that the modified γ-Al_2O_3 which was prepared using the incipient wetness impregnation method can be promoted by the addition of Fe, Co, Ni, Cu and Zn. In most cases (i.e. for Fe-, Co- and Cu-modified catalysts) the enhancement in activity was short-lived, and only the Ni- and Zn-modified catalysts exhibited stable catalytic performance. However, the activities and lifetime of these catalysts was still limited. With the introduction of stringent requirements to reduce the sulfur content in industrial feed gas, the fresh impetus is being given to modifying and improving the existing preparation method of hydrolysis catalyst.

In recent years, the mixed oxides derived from hydrotalcite-like compounds (HTLCs) as catalysts were received much attention in view of their unique properties [14]. HTLCs, also known as layered double hydroxides (LDHs), are a family of anionic clays. The chemical composition can be represented by the general formula: $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M(II) and M(III) is divalent and trivalent cations in the octahedral positions within the hydroxide layers, x is the molar ratio $M(III)/M_{total}$ and its value ranges between 0.17 and 0.33. A^{n-} is an exchangeable interlayer anion [15,16]. HTLCs calcined at high temperatures will lose crystal water, and the interlayer anions and hydroxyl will be removed, too. Therefore, the hydrotalcite-like layered structures will be destroyed, the surface area will increase, and the metal oxides are obtained [17]. Promising applications of these materials have been reported. They can be applied as adsorbents and ion-exchangers because of their large interlayer space and considerable number of exchangeable anions [18–24]. As catalysts, the mixed oxides derived from HTLCs often display good activity owing to their large surface areas, basic properties, high metal dispersions and high thermal stability [25–29].

In our previous studies, we found that the mixed oxide derived from HTLCs is a kind of potential catalysts for the hydrolysis of COS at low temperature [29]. In this paper, we extend our study. A series of Zn–Al HTLCs derived oxides were prepared. The objective of this work was to systematically investigate the effect of calcination temperature, pH, water, and O_2 on hydrolysis of COS at low temperature.

2. Experimental

2.1. Catalyst preparation

The precursors, Zn–Al HTLCs with Zn–Al mole ratio of 2, were synthesized by the co-precipitation method. A solution containing 0.08 mol of $Zn(NO_3)_2\cdot 6H_2O$ (Analytical reagent, Dongsheng Chemical Reagent Factory of Tianjin) and 0.04 mol of $Al(NO_3)_3\cdot 9H_2O$ (Analytical reagent, Dongsheng Chemical Reagent Factory of Tianjin) in 120 ml water was prepared. Under mechanical stirring, the metal nitrates solution was slowly added into the aqueous NaOH (0.28 mol) (Analytical reagent, Zhiyuan Chemical Reagent Factory of Tianjin) and Na_2CO_3 (0.05 mol) (Analytical reagent, Zhiyuan Chemical Reagent Factory of Tianjin) solution. Adjust pH to the required value by the addition of the required drops of HCl solution (Analytical reagent, Zhiyuan Chemical Reagent Factory of Tianjin). After the titration end, the resulting slurry was continuously stirred by the motor stirrer with a speed of 1000 rpm for another 30 min. The resulting slurry incubated at 50 °C in the electric-heated thermostatic water bath for 10 h. The precipitate was washed with distilled water until the pH of the filtrate was around 7, and dried at 60 °C in the dry oven. To produce mixed oxides, the dried samples were calcined at different calcination temperatures for 3 h.

2.2. Characterization

Thermal decomposition of the hydrotalcites was evaluated by thermogravimetric analysis (TG) and differential thermal analysis (DTA) carried out on a ShimadzeDT-40 instrument operating at a 10 °C/min heating rate up to 800 °C. X-ray diffraction (D/MAX-2200) patterns were obtained with a Rigaku diffractiometer operated at 36 kV and 30 mA by using Ni-filtered Cu Kα radiation ($\lambda = 0.15406$ nm) at a rate of 5°/min from $2\theta = 20°$ to 90°. The powdered samples were analyzed without previous treatment after deposition on an agate mortar. The identification of crystalline phases was made by matching the JCPDS files.

2.3. Catalyst testing

Desulfurization tests were performed in a fixed-bed quartz reactor (4 mm i.d × 100 mm length) under atmospheric pressure. For COS hydrolysis, COS from gas cylinder (1% COS in N_2) was diluted with 99.99% N_2 and 0.5% O_2 to the concentration of 1000 mg/m^3. The overall flow rate was controlled using calibrated mass flow controllers (Beijing Sevenstar Electronics Co., Ltd.). The water was introduced using a saturator system. The temperature of the reactor was controlled to 50 °C over its entire length by water-bath with circulating pump, with accuracy ± 1 °C. The concentration of COS and H_2S were analyzed using gas chromatography with a pulsed flame photometric detector (Hubei Huashuo Technology Inc.).

3. Results and discussion

3.1. X-ray diffraction spectrum analysis

The HTLCs structure will be destroyed when it is calcined at high temperatures [17,30].The phase changes of samples are closely associated with the temperatures of their thermal decomposition. To investigate the phase change of catalysts in the thermal decomposition process, XRD patterns of uncalcined HTLCs and HTLCs calcined at different temperatures were obtained (Fig. 1). As shown in Fig. 1, the uncalcined sample exhibits X-ray diffractograms characteristic of hydrotalcite-type compounds: the presence of sharp and intense lines at low values of the 2θ angle, and less intense and generally asymmetric lines at higher angular values. The diffraction reflections around $2\theta = 11$, 23 and 34 correspond to (003), (006), and (009) crystal planes, respectively. The broad diffraction reflections around $2\theta = 35$, 39, 47, 60 and 61 were attributable to (012), (015), (018), (110), and (113) crystal planes. Calcination at 400 °C resulted in the destruction of the HTLCs

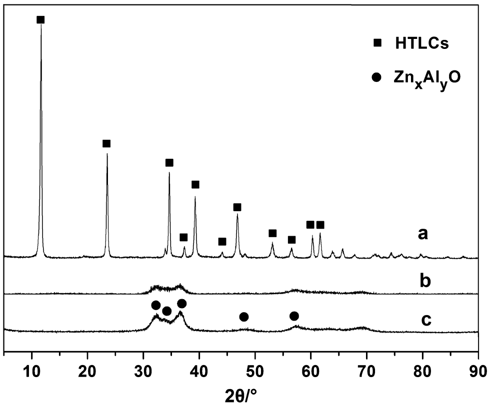

Fig. 1. XRD patterns of (a) uncalcined HTLCs; (b) HTLCs calcined at 400 °C; (c) HTLCs calcined at 500 °C.