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Research paper

Catalytic hydrolysis of COS over calcined CoNiAl hydrotalcite-like compounds modified by cerium

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ABSTRACT

The catalytic performance of COS hydrolysis over calcined CoNiAl hydrotalcite-like compounds (HTLCs) modified by cerium was investigated. All catalysts were prepared by thermal decomposition of hydrotalcite-like precursors synthesized by co-precipitation method and characterized by various technologies. Among all catalysts studied, catalyst CoNiAl-50 exhibited excellent COS conversion. The changes of structural properties, oxidative properties of catalysts and increase of surface defect sites mainly accounted for the enhancements of the catalytic activities with addition of cerium. Element sulfur and the sulfate species accumulated on the surface which might contribute to catalyst poisoning and Ce could affect the formation and content of element sulfur and sulfate.

1. Introduction

The scarcity of conventional fossil fuels and the concern of environmental protection have attracted increasing worldwide interest. Increasing energy utilization and removal of sulfur-containing compounds in feedstocks which account for most of the emissions of toxic and harmful gas are important technologies (Adams and Shachmurove, 2008; Demirbas, 2008; Dicorato et al., 2008; Kissock and Eger, 2008; Zhou et al., 2008). Removal of sulfur-containing compounds is one of the most important technologies for the utilization of various feedstocks. Especially, carbonyl sulfide (COS) which widely exists in natural gas, petroleum gas, water gas and semiwater gas is one of the major components of organic sulfur compounds (Rhodes et al., 2000; Svoronos and Bruno, 2002). Because COS is inactive compared with H_2S, removal of COS is not yet as much of a concern as H_2S. Not only does COS affect the environment by leading to the formation of acid rain, but it also presents problems within industry itself. A trace amount of COS results in the deactivation of catalysts and leads to corrosion of reaction equipment. Besides, untreated COS is transported into the stratosphere, where it can form SO_2 and accelerate photochemical reaction, and it converts into sulfate aerosols eventually (Liu et al., 2008; Sakanishi et al., 2000; Sparks et al., 2008; Williams et al., 1999). Therefore, it is of great significance to remove COS.

Attention has recently been focused on hydrolysis of COS because the hydrolysis products, carbon dioxide and hydrogen sulfide, are much easier to remove than COS (Li et al., 2005). Catalytic hydrolysis of COS follows the reaction:

$$COS + H_2O \rightarrow H_2S + CO_2.$$

Previous papers have been devoted to the study of COS hydrolysis on metal oxides such as Al_2O_3, ZrO_2, TiO_2 or their mixtures (Laperdrix et al., 1998). Among the catalysts studied, those mixed oxides derived from hydrotalcite-like compounds (HTLCs) have not been paid much attention. These compounds may be applied in catalytic fields after thermal decomposition. Heating induces dehydration, dehydroxylation and loss of compensating anions, forming mixed oxides with basic properties, high specific surface area, homogeneous dispersion of the metal ions and a better resistance to sintering than the corresponding supported catalysts (Casenave et al., 2001). Moreover, alumina has been found to be a promising catalyst for hydrolysis of COS, and the catalyst activity can be significantly enhanced by the addition of other metal (Huang et al., 2006; Thomas et al., 2003; West et al., 2001). Based on this background, the M(II)–Al or M(II)–M(II)–Al mixed oxide catalyst for COS hydrolysis was derived from corresponding HTLCs precursors (Ryzhikova et al., 2011; Wang et al., 2011; Yi et al., 2011a, 2011b; Zhao et al., 2012).

More recently, cerium-containing materials have been studied as structural and electronic promoter used for catalysts. It has been shown that, addition of cerium could improve the catalyst redox properties of transitional metals (Ning et al., 2010; Zhao et al., 2008). A study (Zhang et al., 2004) reported that rare earth oxysulfide catalysts were superior to the traditional Al_2O_3 and TiO_2-based catalysts for COS hydrolysis in anti-poisoning of oxygen. In our previous studies, we have shown that CoNiAl, ZnNiAl and ZnNiFe mixed oxides derived

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from corresponding HTLCs were effective catalysts for the hydrolysis reaction (Wang et al., 2011; Yi et al., 2011a, 2011b; Zhao et al., 2012) and the activity was enhanced for ZnNiAl catalyst modified with Ce (Zhao et al., 2010), but we did not study the effect of Ce for other calcined HTLCs. However, the effect of Ce for different HTLCs precursors and corresponding mixed oxide catalysts was different, and it is necessary to study its effect on other catalysts. The purpose of this study is to investigate the effect of Ce on the structural properties and catalytic activity of the CoNiAl mixed oxide catalyst. Moreover, catalyst deactivation was also investigated.

2. Methods and materials

2.1. Catalyst preparation

The precursor HTLCs were prepared by co-precipitation from aqueous solutions reported previously (Wang et al., 2011). A mixture of $Co(NO_3)_2\cdot6H_2O$, $Ni(NO_3)_2\cdot6H_2O$, $Al(NO_3)_3\cdot9H_2O$ and $Ce(NO_3)_3\cdot6H_2O$ ($[Co^{2+}]+[Ni^{2+}]+[Al^{3+}]=0.075$ mol and the molar ratio of Al/Ce is 60, 50, 20, 10, 5) was dissolved in 25 ml distilled water. Unless specified otherwise, the molar ratio of Co/Ni was 0.25 and (Co + Ni)/Al was 2. A second solution containing NaOH (calculated amount required for complete reaction with the divalent and trivalent metal ions) and Na_2CO_3 (0.05 mol) in 50 ml distilled water was prepared. The metal nitrates solution was added to the aqueous alkali slowly under mechanical stirring at 25 °C, and the pH of the solution was adjusted by HCl and Na_2CO_3 to 9. Then the solution was stirred for another 30 min after synthesis. The resulting slurry was aged at 50 °C for 12 h. The precipitate was then filtered with distilled water until the filter liquor attained pH of 7. The resulting solid was dried at 60 °C. To produce mixed oxides, the HTLCs were calcined at 350 °C for 2 h with a heating rate of 5 °C/min. The synthesized samples were named CoNiAl and CoNiAl-X, where X is the Al/Ce molar ratio.

2.2. Characterization

X-ray diffraction (XRD) pattern was obtained with a Rigaku diffractometer operated at 36 kV and 30 mA by using Ni-filtered Cu K_α radiation ($\lambda=0.15406$ nm) at a rate of 5°/min from $2\theta=20°$to 80°. 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 and the crystallinity was calculated by MDI Jade 5.0.

Fourier-transform infrared spectra (FT-IR) measurements were performed on a Thermo Nicolet AVATAR FT-IR 360 instrument. Potassium bromide pellets containing 0.5% of the catalyst were used in FT-IR experiments and 34 scans were accumulated for each spectrum in transmission, at a spectral resolution of 4 cm^{-1}. The spectrum of dry KBr was taken for background subtraction.

The Brunauer–Emmett–Teller (BET) specific surface areas and pore size distribution for the samples were determined by N_2 adsorption using an Autosorb-1-C instrument. The samples were first outgassed at 573 K for more than 12 h before adsorption isotherms were generated by dosing nitrogen (at 77 K) on the catalysts.

X-ray Photoelectron Spectroscope (XPS) (PHI 5500) analysis used Al Kα radiation with energy of Al rake and power of 200 W. Kinetic energies of the photoelectrons were measured by a two-stage spectrometer. The analyzer resolution was 1 eV. An Ar^+ ion gun was used to sputter clean specimen surfaces. The ion energy was set to 1 keV and the sputtering time was 10 min. The photoelectron spectra were calibrated using the C 1s signal detected at a binding energy of 284.8 eV from adventitious carbon. Atomic compositions were calculated with the corrected Scofield coefficients of the transmission function of the analyzer and/or with experimental coefficients determined for a reference compound. The continuum spectrum was fitted according to the Gaussian–Lorentzian files.

2.3. Measurement of catalytic activity

The details of the catalyst activity test were well described in the previous work (Wang et al., 2011) and only brief description was given here. Gaseous COS (1% COS in N_2) from a gas cylinder was introduced with N_2 (99.99%) as carrier flow and they were completely mixed in a mixing chamber before the reactor. The flow rates of air were adjusted by a set of mass flow controllers. H_2O was introduced through a saturator controlled by a thermostatic water bath and the relative humidity of the reaction gas was adjusted by changing the temperature of the water bath. The gas containing 1000–1100 $mg\cdot m^{-3}$ COS and 2.67% relative humidity passed through the catalyst bed at a rate of 20.93 $ml\cdot min^{-1}$, with the gas hourly space velocity (GHSV) being 2000 h^{-1}. In view of environment, the off-gas was absorbed by NaOH solution. The temperature of reactor was controlled at 50 °C over its entire length by water-bath with circulating pump, with accuracy ±1 °C. The conversion of COS was determined by analyzing the inlet and outlet concentrations of COS using a GC-508 gas chromatography with a flame photometric detector (FPD). In this investigation, COS conversion was selected to value the catalytic activity and calculated as follows:

$$\text{COS conversion }(\%)=\frac{\text{COS}_{\text{inlet}}-\text{COS}_{\text{outlet}}}{\text{COS}_{\text{inlet}}}\times100\%$$

where, COS_{inlet} ($mg\cdot m^{-3}$) and COS_{outlet} ($mg\cdot m^{-3}$) are the concentrations of COS measured at the inlet and outlet of the reactor.

3. Result and discussion

3.1. Catalytic activity

Fig. 1 showed the catalytic performance of a series of catalysts. As shown in Fig. 1, there were significant differences between the Ce-free and Ce-containing catalysts. For sample of CoNiAl, a 99% conversion was observed for about 210 min. When sample of CoNiAl-X was used, the removal efficiency was different along with Ce loading amounts. The conversion initially increased with the Ce content increased (from CoNiAl-5 to CoNiAl-50), but then decreased with the further increase of Ce content. The efficiency reached the maximum at CoNiAl-50 and it was 550 min when the COS conversion was sustained above 99%. This value is significantly higher than other calcined HTLCs or modified by Ce for COS hydrolysis at low temperature (Wang et al., 2011; Yi et al., 2011a, 2011b; Zhao et al., 2010; Zhao et al., 2012). The reason may be that the effect of Ce for different HTLCs and

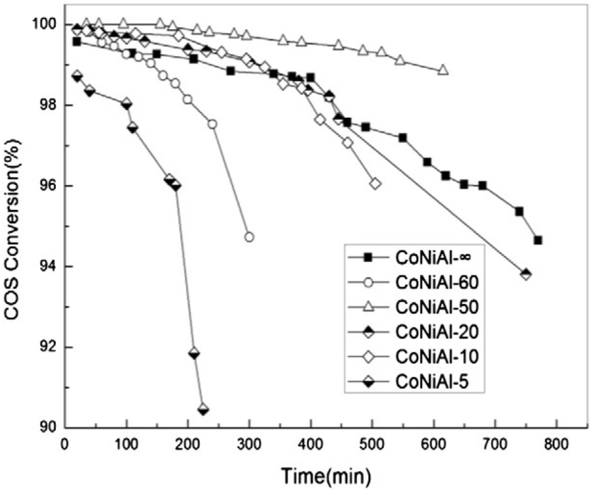

Fig. 1. COS conversion over CoNiAlCe with various Ce contents. Reaction condition: 1016 $mg\cdot m^{-3}$ COS, 50 °C, 2000 h^{-1}, relative humidity 2.67%, N_2 to balance.