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ARTICLE

Oxygen Poisoning Mechanism of Catalytic Hydrolysis of OCS over Al_2O_3 at Room Temperature

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Abstract: The oxygen poisoning mechanism of the catalytic hydrolysis of carbonyl sulfide (OCS) over alumina at room temperature was investigated using *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS), XRD, BET, and ion chromatograph (IC). The surface hydroxyl (−OH) species triggered the catalytic hydrolysis of OCS on Al_2O_3, with the formation of surface hydrogen thiocarbonate ($HSCO_2^-$) species as a key intermediate. Surface SO_4^{2-} was identified with *in situ* DRIFTS and IC. It was found that the accumulation of sulfate on catalyst led to the poisoning of Al_2O_3 in the presence of oxygen.

Key Words: Carbonyl sulfide; Catalytic hydrolysis; Oxygen poisoning; Sulfate; Alumina

Carbonyl sulfide (OCS) is commonly existed in coke oven gas, coal making gas, natural gas, petroleum refining exhaust gases, the flue gas, vechicle exhaust and Claus tail gases[1−3]. In the processes of manufacturing, OCS not only leads to corrosion of the reaction equipments but also results in the deactivation of catalysts[3,4]. OCS can be transported into the stratosphere, where it is converted into sulfate aerosols through photooxidation, and thus it has an important impact on the environment[5,6]. The main technologies for OCS removal include catalytic hydrolysis, oxidation conversion, and hydrogenation conversion, etc[7]. Among these methods, catalytic hydrolysis was the most principal technology for the removal of OCS in the tail gases[1]. Catalytic hydrolysis of OCS follows the reaction:

$$OCS+H_2O \rightarrow CO_2+H_2S \qquad (1)$$

Recently, hydrolysis catalyst with high activity for the removal of OCS at low temperature or normal temperature has attracted considerable interest of researchers[1,7−10]. The previous researches showed that at high temperature, the formation of elemental sulfur and sulfate on the surface of catalyst is the main reason that leads to the deactivation of catalyst for OCS hydrolysis; the higher the temperature, the faster the deactivation of catalyst[11−14]. Alumina (Al_2O_3) is a common catalyst carrier and activate component for the catalytic hydrolysis of OCS [1,8−15]. Therefore, it is of great significance to study the sulfate formation mechanism of OCS over Al_2O_3 to improve the resistance of catalyst to sulfate poisoning. The catalytic hydrolysis of OCS over Al_2O_3 at room temperature has a potential in application. In this study, different crystal types of Al_2O_3 samples were chosen to investigate the hydrolysis of OCS at room temperature. The products and intermediates of OCS catalytic hydrolysis over Al_2O_3 at room temperature were inspected using *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), ion chromatograph (IC), etc. The effects of the calcination temperature of the Al_2O_3 on the oxygen poisoning of catalyst in the catalytic hydrolysis of OCS at room temperature were studied. By combining the results of the experiments, the oxygen poisoning mechanism of the catalytic hydrolysis of OCS over Al_2O_3 was proposed.

1 Experimental

1.1 Preparation and characterization of catalyst

The samples of Al_2O_3-A, Al_2O_3-B, and Al_2O_3-C were prepared directly from boehmite (AlOOH) powder (Shandong Aluminum Corporation, China), stirred with deionized water

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for 2 h, dried at 373 K for 3 h, and calcined at 573, 873, and 1473 K for 3 h, respectively. The catalyst was crushed into 20–40 meshes particles for experimental use.

The X-ray diffractometry of samples was implemented using a computerized Rigaku D/Max-II Diffractometer (Cu K_α radiation sources, the tube voltage of 40 kV, the tube current of 80 mA, the scanning speed of 4 (°)·min^{-1}, scanning range of 10°–90°). The Brunauer-Emmett-Teller (BET) surface areas of the samples were obtained using Micromeritics ASAP 2010 automatic equipment.

1.2 Evaluation of the catalytic hydrolysis activity of OCS over Al_2O_3

The evaluation reactions of OCS catalytic hydrolysis over Al_2O_3 were conducted in a fixed-bed quartz reactor (ϕ6 mm×150 mm). The concentrations of OCS were determined by an infrared spectroscopy (Nicolet NEXUS 670) equipped with a 2 m optical path gaseous chamber. Prior to the activity evaluation test, the Al_2O_3 catalyst samples were pretreated by heating in an oxygen flow at 373 K for 3 h. The OCS used in the experiments was the 2% OCS (OCS/N_2) standard gas (Scott Specialty Gases Inc., American). The other reactant gases were the cylinder gas, which has purity higher than 99.999%. The water vapor was introduced by N_2 pass through a water saturated generator in a water bath.

The reaction conditions were as follows: φ(OCS)=0.03%, $\varphi(H_2O)$=0.24%, $\varphi(O_2)$=0, 2%, 10%, balanced with N_2. The masses of the catalysts used in the activity evaluation experiments were 0.6 g, and the total gas flow rate was 100 mL·min^{-1} (GHSV (gas hourly space velocity) was 2500 h^{-1}). The reaction temperature was 298 K.

1.3 Analysis of the sulfate generated over Al_2O_3 by IC

The sulfate formed over Al_2O_3 from OCS was converted into water soluble sulfate and the quantitative analysis was determined using ion chromatograph (IC). 1.2 g of the Al_2O_3 sample was placed in the reactor, preoxidized by heating at 573 K in a 100 mL·min^{-1} O_2 flow gas for 3 h, cooled to 298 K, and exposed to 100 mL·min^{-1} 0.05% OCS + 21% O_2 flow gas for a given time. The reacted Al_2O_3 sample was washed with 100.00 mL deionized water and transported into a 500 mL dried conical flask, ultrasonically extracted for 30 min. The extracted liquid was filtered through a 0.45 μm filter. The concentration of water soluble sulfate in the filtrated solution was analyzed by IC.

The eluant consisted of 3.5 mmol·L^{-1} Na_2CO_3/1 mmol·L^{-1} $NaHCO_3$ passed through the IC system (Dionex, CA) at a flow rate of 1.2 mL·min^{-1}. The injection volume of the liquid sample was 25 μL. The solution was filtered through a 0.2 μm filter before entering the analytical column. The concentration of sulfate was in linear correlation with its peak area in the concentration range of 1–40 mg·L^{-1} (R^2=0.9997); thus, we can calculate the concentration of sulfate on the basis of its peak area.

1.4 *In situ* DRIFTS experiment

In situ DRIFTS consists of *in situ* DRIFTS spectra apparatus equipped with a MCT detector (NEXUS670, Nicolet Co. USA), an *in situ* diffuse reflection chamber, and attachments. The component, pressure, and temperature of gas in the *in situ* diffuse reflection chamber can be precisely controlled through the mass flow controllers and a temperature controller[16].

The procedures of catalyst preoxidized treatment are described as follows: the Al_2O_3-A sample was heated in the *in situ* infrared cell in 100 mL·min^{-1} O_2 at 573 K for 3 h. The Al_2O_3-B and Al_2O_3-C samples were pretreated in the *in situ* infrared cell by heating in 100 mL·min^{-1} O_2 at 873 K for 3 h. The prereduced treatment of catalyst: the Al_2O_3-A sample was pretreated in the *in situ* infrared cell by heating in 100 mL·min^{-1} H_2 at 573 K for 3 h. The reference spectrum was recorded after the pretreated sample cooled to 298 K and the absorption of water vapor was subtracted as background. The sample was exposed to 100 mL·min^{-1} reactant gas at room temperature, and the information of the surface species was detected using NEXUS670 *in situ* DRIFTS spectra apparatus in the wavenumber range of 650–4000 cm^{-1} with 4 cm^{-1} of resolution and 100 scan times.

1.5 Quantitative analysis of gas-phase OCS concentration

When the concentration of OCS gases in the IR gaseous chamber of the activity evaluation test reached an equilibrium, the integrated areas of the absorption peak of gaseous OCS located at 2071 cm^{-1} and 2052 cm^{-1} have a linear correlation with the concentration of OCS gas (R^2=0.9990) in the range of 0–0.1%, to achieve the quantitative analysis of OCS concentration.

2 Results and discussion

2.1 Sample characterization

Fig.1 shows the XRD patterns of the crude AlOOH and Al_2O_3 calcined at different temperatures. It can be seen that the Al_2O_3-A sample still exists mainly as AlOOH after the AlOOH was calcined at 573 K for 3 h. The crystal type of the sample changed gradually with rising calcination temperature. The Al_2O_3 samples mainly exist as the crystal type of γ-Al_2O_3 (2θ=67°, 46°, and 37°)[17] and α-Al_2O_3 (2θ=43°, 35°, and 57°)[18,19] after AlOOH was calcined at 873 and 1473 K, respectively. This transformation of crystal structure is consistent with the report in the literature[20].

The results of BET measurement showed that the surface areas of AlOOH, Al_2O_3-A, Al_2O_3-B, and Al_2O_3-C samples were 318, 277, 257, and 12 m^2·g^{-1}, respectively. After the calcination treatment, the surface structure and the bulk structure