



## Enhancement effects of ultrasound assisted in the synthesis of NiAl hydrotalcite for carbonyl sulfide removal



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### ABSTRACT

Ultrasonic effect in the synthesis of catalysts of NiAl oxides prepared starting from the coprecipitation method of a hydrotalcite structure was evaluated in this work. Removal of carbonyl sulfide (COS) at low temperature over the hydrotalcite-derived oxides was studied. The samples were characterized by X-ray Diffraction (XRD), scanning electron microscope (SEM), N<sub>2</sub> adsorption/desorption techniques, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and CO<sub>2</sub> temperature-programmed desorption (TPD). It is found that hydrotalcite treated with ultrasonic has smaller average crystallite size and higher particle dispersion compared to hydrotalcite without ultrasonic treatment. As a result, mixed oxides derived from hydrotalcite treated with ultrasonic show more developed pore structure which is good for the physical adsorption of gaseous pollutant. The result of desulfuration test showed that removal efficiency of COS on the NiAl mixed oxides prepared by ultrasonic method (30 min) is greater than that on the catalyst prepared without the ultrasonic irradiation assistance with the same aging time. One important reason for the high activity is that when the ultrasonic is used the number of weak basic sites (OH<sup>-</sup> groups) and moderate basic sites (M–O) was increased, whereas the number of strong basic sites (O<sup>2-</sup>) was decreased. Therefore, ultrasonic treatment promoted the COS hydrolysis and suppress the poisoning of the catalyst.

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## 1. Introduction

Carbonyl sulfide (COS), widely exists in natural gas, petroleum gas, and water gas, is unique among the sulfur-containing impurities in hydrocarbon feed stocks due to its odorless, tasteless and colorless characters. Trace amount of COS can result in the deactivation of catalysts and lead to corrosion of reaction equipment [1–3]. Furthermore, not only does COS provides economic problems, but also affects the environment. Photolysis of COS is the main source of stratospheric sulfate layer [4,5]. Thus, deep removal of COS is in high demand.

COS is difficult to be removed efficiently by the conventional method of desulphurization. An alternative technology has to be used for the removal of COS, and this is based on the formation of H<sub>2</sub>S by hydrolysis: COS + H<sub>2</sub>O = H<sub>2</sub>S + CO<sub>2</sub>. Liu et al. [6] studied the heterogeneous reaction of COS on mineral oxides. The results

showed that the activity series for heterogeneous oxidation of COS decrease in the following sequence: Al<sub>2</sub>O<sub>3</sub> ≈ CaO > MgO > TiO<sub>2</sub> ≈ ZnO > Fe<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>. The specific surface area and surface basicity of these oxides have great effect on the catalytic activity. There are two steps in the COS removal. The first step is the catalytic hydrolysis of COS. In this step, basic sites (surface-exposed hydroxyl groups and M–O pairs) are active centers for hydrolysis. Secondly, H<sub>2</sub>S is oxidized to sulfate, metal sulfide, and elemental sulfur by oxygen-containing functional groups (M–O pairs and O<sup>2-</sup>). The hydrolysis of COS is basic-catalyzed by surface-exposed hydroxyl groups or metal sites. The oxidation of hydrogen sulfide also requires metal sites. This suggests that the materials which can provide abundant and active acid/base sites having a great applying potentiality.

Hydrotalcite-like compounds (HTLCs), also known as layered double hydroxide (LDH), are a family of anionic clays [7–12]. The chemical composition can be represented by the general formula: [M(II)<sub>1-x</sub>M(III)<sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>(A<sup>n-</sup>)<sub>x/n</sub>·mH<sub>2</sub>O, 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(III) + M(II) and its value ranges between 0.2 and 0.4. A<sup>n-</sup> is an exchangeable

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interlayer anion. The structure of HTLCs is similar to that of brucite where each  $Mg^{2+}$  ion is octahedrally surrounded by six OH ions and the different octahedra share edges to form infinite sheets. In the process of roasting, HTLCs can lose crystal water and the interlayer anions. Mixed oxides derived from the HTLCs received much attention because of the unique properties. Owing to their amazing properties, hydrotalcite-derived oxides (HTO) have received increased interest in anion exchange media, adsorbents, catalysis, drug delivery systems, and so forth [13–18].

In the previous studies, we have reported that mixed oxide derived from HTLCs is an effective catalyst for the COS removal, and the preparation condition (pH values, synthetic temperature, and calcination temperature) has great influence on the activity of the catalysts. However, the activity of the catalyst is not satisfactory.

Ultrasonic (US) technology has been applied to the rapid synthesis of inorganic solids and organic synthetic reactions. It was used to increase the metallic dispersion and to allow a considerable decrease the time in the modification process without deterioration of the final material properties. For instance, ultrasonic radiation synthesis in the preparation of not only can shorten the synthetic time, but also can make the resultant samples to possess more even pore sizes and larger surface areas [19]. Xie et al. reported that ZnAl-HTLCs with small particle sizes and narrow particle size distributions can be obtained by the ultrasonic crystallization method [20].

In this work, we have attempted the synthesis of NiAl HTLCs using ultrasonic as an aging method to remove COS, with the aim of increasing both number and base strength of the active sites. The samples were characterized by X-ray Diffraction (XRD), scanning electron microscope (SEM),  $N_2$  adsorption/desorption techniques, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and  $CO_2$  temperature-programmed desorption (TPD) in order to explore how ultrasonic affects the desulfurization performance in contrast to mechanical stirring.

## 2. Experimental methods

### 2.1. Catalyst preparation

NiAl HTLCs with a Ni/Al molar ratio of 3 were synthesized by the co-precipitation method. A schematic of the catalyst preparation setup is shown in Fig. 1. At first, the solution containing NaOH (0.16 mol) and  $Na_2CO_3$  (0.05 mol) in 200 ml water was prepared. Put the solution in a two mouth flask which was placed in the SMART-02B ultrasonic cleaner (200 W, 40 kHz, SMART Ultrasonic

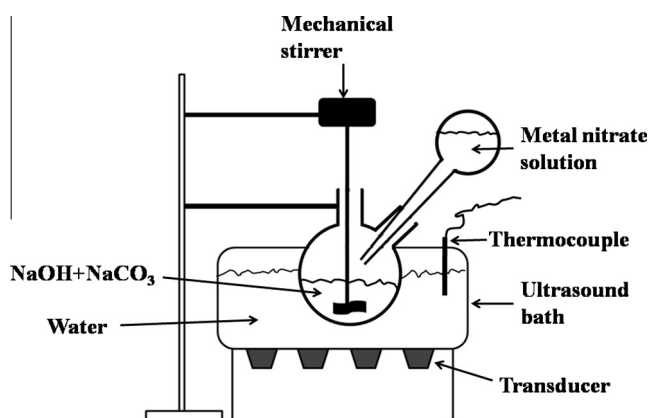


Fig. 1. Schematic of the preparation equipment of the catalysts.

Technology Co., Ltd. China). 2/3rd of bath volume of the ultrasonic cleaner was filled with water, which acted as medium for transmission of ultrasonic. A solution containing 0.06 mol of  $Ni(NO_3)_2 \cdot 6H_2O$  and 0.02 mol of  $Al(NO_3)_3 \cdot 9H_2O$  in 100 ml water was prepared. Under ultrasonication and mechanical stirring, the metal nitrates solution was slowly added into the aqueous NaOH (0.16 mol) and  $Na_2CO_3$  (0.05 mol) solution. Adjust the pH to 10 by the addition of the required drops of HCl solution. After the titration end, the resulting slurry was stirred continuously for another 30 min. In the whole experiment, the temperature was kept at  $50 \pm 1$  °C. 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. The sample is denoted as NiAl-UHTLCs. To produce mixed oxides, the dried sample was calcined in air at 400 °C for 3 h, and this sample is denoted as NiAl-UHTO.

As a contrast, another sample was synthesized by the co-precipitation method without the ultrasonic irradiation assistance, which is denoted as NiAl-HTLCs and NiAl-HTO.

### 2.2. Activity tests

Desulfurization performance tests were carried out in a fixed-bed reactor, under conditions described elsewhere [21,22]. Inlet concentration of COS was set at 200 ppm. Gas flow was controlled by mass flowmeter. The total gas flow rate was 20 ml/min, with a catalyst volume of 0.2 ml. Water vapor was introduced by a water saturator. The water vapor content can be changed by adjusting the temperature of saturator. The reaction temperature was set to 60 °C. Concentration of COS was determined by gas chromatograph.

The conversion was calculated using

$$\text{Conversion} = \left( 1 - \frac{C_{\text{out}}}{C_{\text{in}}} \right) \times 100\%$$

where  $C_{\text{in}}$  and  $C_{\text{out}}$  is the concentration of COS in the inlet gas and outlet gas, respectively.

### 2.3. Catalyst characterization

XRD patterns were obtained with a Rigaku D/MAX-2200 diffractometer operated at 36 kV and 30 mA by using Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 0.15406$  nm) at a rate of  $5^\circ/\text{min}$  from  $2\theta = 5^\circ$  to  $80^\circ$ . The identification of crystalline phases was made by matching the JCPDS files. The integral intensity and full width in half maximum (FWHM) of the (003) diffraction lines were evaluated in order to compare the crystallinity of samples.

XL30ESEM-TMP (Poland) type SEM was used to obtain high-resolution images of the catalysts, which was used for microstructure observation of the surface.

Physisorption of  $N_2$  was performed at 77 K using a NOVA2000e (Quanta chrome instruments) surface area analyzer after the samples were degassed for 2 h at 298 K. The surface area and pore size distribution were calculated by the Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Hallender (BJH) method, respectively.

A Nicolet IS 50 FTIR was used to verify the presence of functional groups in the catalyst. The infrared spectra were recorded both over the wave number range from 400 to  $4000\text{ cm}^{-1}$ .

XPS analysis was applied to determine the surface chemical composition and functional groups. XPS was performed on ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al  $K\alpha$  radiation. Wide scans were performed from 1100 eV to 0 eV with a dwell time of 100 ms and steps of 1 eV. Narrow scans were performed with steps of 0.05 eV if the range  $<15$  eV

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