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Full Length Article

Effects of preparation methods on the property and hydrodesulfurization activity of NiAlZrW catalysts derived from tungstate intercalated NiAlZr layered double hydroxides

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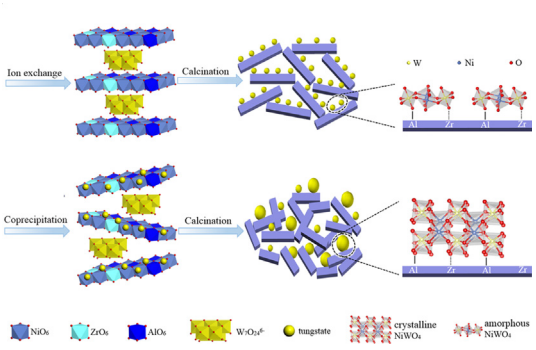
GRAPHICAL ABSTRACT

Tungstate intercalated NiAlZr layered double hydroxides (LDHs) are synthesized by an ion exchange (IE) method and a coprecipitation (CP) method. They are calcined and sulfurized as HDS catalysts. The introduction of Zr by the IE method facilitates the formation of highly dispersed and amorphous $NiWO_4$ species with the improved reducibility and sulfidability, resulting in the enhanced activity. However, the CP method favors the formation of crystalline $NiWO_4$ species which further grow into big crystallites with the addition of Zr, leading to the poorer reducibility, sulfidability and activity.



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ABSTRACT

A series of tungstate intercalated NiAlZr layered double hydroxides (LDHs) with various Zr contents were synthesized by an ion exchange method and a coprecipitation method, respectively. They were further calcined and used as hydrodesulfurization (HDS) catalysts. The effects of preparation methods on the property and HDS activity of catalysts were investigated. It is found that the introduction of Zr by the ion exchange method facilitates the formation of amorphous and well dispersed $NiWO_4$ species, because the highly ordered layered structure can be well retained after calcination, acting as support and separator to disperse $NiWO_4$ species and prevent them from aggregation. Moreover, the reducibility and sulfidability of catalysts are improved, because the substitution of Al by Zr in the brucite-like layers could decrease the strong W—O—Al linkages and hence weaken the metal-support interaction. Therefore, the HDS activity and hydrogenation selectivity for dibenzothiophene are significantly improved with the increase in Zr content up to Zr/Al ratio of 0.3/0.7 whose HDS rate constant is 55.7% higher than that of the Zr-free catalyst. However, the coprecipitation method leads to the formation of crystalline $NiWO_4$ species which grow into bigger crystallites with the addition of Zr. This may be attributed to the lower crystallinity of LDHs and the formation of $NiWO_4$ salt during the coprecipitation process. As the Zr content increases, the reducibility and sulfidability of catalysts are declined remarkably, due to

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the crystal growth and aggregation of $NiWO_4$. Therefore, the introduction of Zr by the coprecipitation method decreases the HDS activity of catalysts.

1. Introduction

In the past decades, increasing environmental concerns and stringent vehicle exhaust emission regulations require the considerable reduction of the sulfur content in fuels. Hydrodesulfurization (HDS) is the most widely used technology in refinery to meet the ever-stricter sulfur limitation. To achieve the deep HDS, the removal of polyaromatic sulfur compounds such as dibenzothiophene (DBT) and its alkyl substitutions which are the refractory sulfides in diesel [1], should be further improved. As a result, intensive efforts have been devoted to develop novel transition metal sulfides HDS catalysts.

Layered double hydroxides (LDHs) constitute an important class of anionic lamellar clays with the general formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}mH_2O$. Herein, M^{2+} and M^{3+} are divalent and trivalent metal cations octahedrally surrounded by oxo bridges and hydroxyl groups in the brucite-like layers; A^{n-} are the anions in the interlayer gallery to compensate the excessive positive charges of the layers [2]. Due to the versatility of metal cations in the layers joined with the exchange ability of anions in the interlayer, LDHs have numerous potential applications as catalysts, catalyst supports, ion exchangers and adsorbents, etc [2,3]. Recently, LDHs has attracted attentions as catalyst precursors or catalysts for HDS [4–8], because of their unique layered structure and large surface area. The most common method to introduce active metals into LDHs is to incorporate Ni and/or Co in the layers and to intercalate tungstate and/or molybdate into the interlayer. After calcination and sulfidation, the multi-metallic HDS catalysts can be achieved. Faro Jr's group [4–6] synthesized molybdate and/or tungstate-intercalated CoMgAl and NiAl LDHs as precursors of HDS catalysts. Li's group [7,8] prepared a series of lamellar NiAlMoW, NiAlZnMoW and NiZnMoW HDS catalysts using LDHs or layered hydroxide salts as precursors. They found that high contents of active metals can be well dispersed on the catalysts and more stacked metal sulfides active phases can be formed, leading to the improved HDS activity.

It is proved that Zr can improve the performance of HDS catalysts by weakening the interaction between active metals and alumina support and enhancing the stability of catalysts [9]. In our previous work [10], a series of tungstate intercalated NiAlZr LDHs were synthesized via an ion exchange method. The as-synthesized LDHs were further calcined at 450 °C to obtain NiAlZrW catalysts with various Zr contents. The results demonstrated that Zr enabled the formation of highly dispersed $NiWO_4$ species and improved the reducibility, resulting in the significant improved HDS activity for DBT and a real diesel feed, when compared to a Zr-free catalyst and a NiW/Al_2O_3-ZrO_2 catalyst prepared by an impregnation method.

The properties of LDHs were strongly related to the preparation methods. Besides the ion exchange method, the coprecipitation method is also a commonly used method for synthesizing LDHs. Moreover, it can offer much less synthesis time and higher efficiency. Polyoxometallate (POM) intercalated LDHs directly synthesized by the coprecipitation method has been reported in literature [11,12].

In the present work, a series of tungstate intercalated NiAlZr LDHs with different Zr contents were synthesized by the ion exchange and a coprecipitation method, respectively. They were further calcined and used as HDS catalysts. The LDHs and catalysts are characterized and tested by HDS of DBT, in order to investigate the effects of preparation methods on the properties and activity of catalysts.

2. Experimental

2.1. Catalysts preparation

NiAlZr nitrate LDHs were used as precursors. The detailed synthesis procedure can be found in the previous report [10]. The Ni/(Al + Zr) atomic ratio was kept at 2 while the Zr/Al atomic ratio was varied from 0/1 to 0.4/0.6. The as-synthesized LDHs were denoted as $Ni_2Al_{1-x}Zr_x$-N, in which x represents the atomic ratio of Zr/(Al + Zr).

For the ion exchange method, tungstate intercalated NiAlZr LDHs were prepared by the following procedure. First, 2 g $Ni_2Al_{1-x}Zr_x$-N and 75 ml decarbonated and deionized water were added in a flask equipped with a condenser and a thermometer. Second, the mixture was stirred at 80 °C for 1 h to swell the layer. Third, 5.5 g $Na_2WO_4{\cdot}2H_2O$ dissolved in 75 ml water was added into the flask and the pH value of the mixture was adjusted to 5.5 by 2% HNO_3 solution. Fourth, the mixture was stirred and refluxed at 80 °C for 12 h. Finally, the products were filtrated, washed with water and then dried under vacuum at 80 °C for 6 h. The corresponding LDHs were denoted as IE-$Ni_2Al_{1-x}Zr_x$-W.

For the coprecipitation method, 0.2 M $Na_2WO_4{\cdot}2H_2O$ solution was added into a flask and its pH value was adjusted to 4.5. A mixed salt solution containing $Ni(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $ZrO(NO_3)_2{\cdot}2H_2O$ with the total metal cations concentration of 0.5 M and 1 M NaOH solution were simultaneously added into the flask under vigorously stirring. The addition speed was carefully controlled to keep the pH value of the mixture at 6. After that, the mixture was further stirred for 1 h and then was transferred into an autoclave at 100 °C for 12 h. The solid products were filtrated, washed with water and dried under vacuum at 80 °C for 6 h. The corresponding LDHs were denoted as CP-$Ni_2Al_{1-x}Zr_x$-W.

NiAlZrW catalysts were obtained by calcining the above LDHs at 450 °C for 4 h under static air in a muffle furnace and denoted as IE-$Ni_2Al_{1-x}Zr_x$W or CP-$Ni_2Al_{1-x}Zr_x$W.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were recorded on a X'Pert Pro MPD diffractor (PANalytical, The Netherlands) using Cu Kα radiation source operated at 40 kV and 40 mA in the 2θ range of 5–70° with a step of 0.02° and a counting time of 12 s per step.

Fourier transform infrared (FT-IR) spectra were measured at room temperature taking KBr as the reference in the range of 500–4000 cm^{-1} on a WQ520 spectrometer (Beifen, China).

Raman spectra were recorded on Micro IM-52 (Oceanoptic, USA) spectrometer equipped with He-Ne laser source. The laser line at 785 nm with an output of 11 mW was used as exciting source.

Scanning electronic micrograph (SEM) was carried out on an EVOMA-15 (Zeiss, Germany) instrument. The samples were dispersed ultrasonically in ethanol, and then a few drops of the suspension were deposited on a brass holder and coated with gold before examination.

Specific surface area and pore volumes of the samples were analyzed by the N_2 adsorption-desorption method at liquid nitrogen temperature using a Quadrasorb SI analyzer (Quantachrome, USA). Prior to the analysis, the samples were degassed at 200 °C for 6 h.

The compositions of samples were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a 7300 V instrument (PerkinElmer, USA).

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher K-Alpha spectrometer (Thermo Fisher, USA) using Al Ka