



Short communication

MgAl-LDO mixed oxide derived from layered double hydroxide: A potential support for CoMo sulfur-resistant water–gas shift catalyst



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ABSTRACT

A series of Mg–Al layered double oxides (MgAl-LDOs) with different Mg/Al molar ratios (Mg/Al = 3–6) was synthesized by calcination of Mg–Al layered double hydroxides, and further used to prepare CoMo water–gas shift (WGS) catalysts by incipient-wetness impregnation method. The as-synthesized CoMo/MgAl-LDO catalysts were investigated by systematically physicochemical characterizations. The CoMo/MgAl-LDO (Mg/Al = 5) catalyst showed much higher catalytic activity than a commercial CoMo/MgAl₂O₄ catalyst, indicating the MgAl-LDOs can be a potential support for the CoMo catalyst. H₂-TPR and H₂S-TPS studies suggest that the Mo species are easier to be reduced and thus more sulfide phases are formed on CoMo/MgAl-LDO (Mg/Al = 5) catalyst.

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1. Introduction

The coal gasification followed by water–gas shift (WGS) is one of the most important processes for the large-scale production of hydrogen [1,2]. Since certain amount of sulfur can be involved in the gasification gases, a sulfur-resistant WGS catalyst with high shift activity is strongly desired under such application [3]. One typical example of sulfur-tolerant WGS catalyst is the CoMo catalyst supported by Al₂O₃ or MgAl₂O₄ [4], which is also known as HDS (hydrodesulfurization) catalyst in hydrotreating processes [5]. When used as a WGS catalyst, the nature of the support is of great importance to CoMo catalyst, since it influences not only the catalytic activity but also the stability under high-temperature, high-pressure and hydrothermal conditions. Therefore, great efforts have been devoted to developing suitable support for CoMo sulfur-resistant WGS catalyst [6].

The Mg–Al layered double oxide (MgAl-LDO), post-calcination product of the Mg–Al layered double hydroxide (MgAl-LDH), is a kind of widely used sorbent material due to its large surface area, high thermal stability, and considerable number of Brønsted basic sites [7–10]. The MgAl-LDHs are a class of lamellar compounds which consist of positively charged brucite-like host layers and hydrated exchangeable anions. The brucite-like host layers consist of divalent (Mg²⁺) and trivalent (Al³⁺) metal cations that can be changed not only in quantity but also in kinds [11]. Especially, the change of di- and trivalent metal cations

in LDHs can affect the structure and electrical affinity of the obtained LDOs, thus changing the catalytic performance of LDO materials [11].

In this work, a series of MgAl-LDO supports were synthesized through calcining the MgAl-LDHs with different Mg/Al molar ratios in the air, and further used to prepare a set of catalysts with incipient-wetness impregnation method. The as-prepared CoMo/MgAl-LDO catalysts were systematically investigated with a series of physico-chemical characterizations. The catalytic performance of the CoMo/MgAl-LDO catalysts was evaluated in WGS reaction, and compared with that of a commercial CoMo/MgAl₂O₄ catalyst. Herein we report that the MgAl-LDO is a potential support for CoMo sulfur-resistant WGS catalyst, and the Mg/Al molar ratio has a significant effect on the catalytic activity of CoMo/MgAl-LDO catalysts.

2. Experimental

2.1. Preparation of MgAl-LDO supports

Mg–Al layered double hydroxides were prepared by the co-precipitation method. The mixed aqueous solution of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O was added under stirring into a beaker containing an aqueous solution of sodium carbonate at room temperature. The pH of the solution was adjusted and kept at 10 ± 0.5 with an aqueous solution of sodium hydroxide. The resulting suspension was then aged at 90 °C for 24 h. Then the resulting precipitate was filtered and washed several times with de-ionized water. At last the precipitate was dried at 100 °C for 12 h and calcined at 700 °C for 4 h with a rate of 3 °C/min in a

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static air atmosphere. The obtained MgAl-LDO support was pressed into a disk, crushed and sieved to particles with 20–40 mesh size.

2.2. Preparation of CoMo/MgAl-LDO catalysts

The catalysts were prepared by incipient wetness impregnation over MgAl-LDO supports. Typically, 5 g MgAl-LDO support (20–40 mesh) was impregnated with aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ to give 1 wt.% CoO and 7 wt.% MoO_3 . The obtained slurry was aged for 12 h at room temperature, followed by drying for 4 h at 100 °C and calcination in air at 450 °C for 2 h. For comparison, a Co/MgAl-LDO reference catalyst was prepared by the same procedure with the same CoO loading.

2.3. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded by a PANalytical X'Pert spectrometer using $\text{Co K}\alpha$ radiation ($\lambda = 0.179 \text{ nm}$) at a scanning rate of $0.12^\circ/\text{min}$. The metal content in each precipitate was determined by inductively coupled plasma (ICP) on an OPTIMA 8000 (PerkinElmer) after the sample was completely dissolved in diluted hydrochloric acid. The BET surface area and pore volume were measured using nitrogen adsorption at 77 K on a Micromeritics ASAP 2020 instrument.

The temperature-programmed reduction (TPR) measurements were performed on a Micromeritics Autochem 2920. First, 0.0500 g catalyst was pre-treated with pure He at 300 °C for 30 min and cooled to room temperature. Then, the sample was heated from the room temperature to 900 °C ($10^\circ/\text{min}$) in a 10 mL/min 10% H_2/Ar mixture. The consumption of H_2 was analyzed by a TCD detector. The temperature-programmed sulfidation (TPS) patterns were registered on a Micromeritics Autochem 2920. Around 200 mg (precisely weighted) catalyst was firstly pre-treated with pure Ar at 300 °C for 30 min. Then the samples were sulfided in 30 mL/min 5% $\text{H}_2\text{S}/\text{N}_2$ from room temperature to 600 °C with a heating rate of $10^\circ/\text{min}$. The evolution of H_2S during sulfidation was recorded by a TCD detector.

2.4. Catalytic activity and stability

The activity and stability of CoMo/MgAl-LDO catalysts in WGS were measured on a vertical fixed-bed micro reactor with 5 ml oxidic catalyst (20–40 mesh). Prior to the test, the catalysts were sulfided in a mixture of $\text{CO}/\text{H}_2/\text{CS}_2$ at 350 °C for 1 h. The catalytic activity measurements were carried out under the condition of reaction pressure of 0.15 MPa in the temperature range 200–450 °C with the feed gas composition 26 vol.% CO, 54 vol.% H_2 , 20 vol.% CO_2 , space velocity 2000 h^{-1} and steam/gas ratio 1. The catalytic stability was tested at 400 °C while keeping the other parameters constant. The steady-state conversion of CO was analyzed by an on-line GC equipped with a TCD detector. The catalytic activity was expressed by the CO conversion:

$$X_{\text{CO}} = [(1 - V_{\text{CO}}/V_{\text{CO}})/(1 + V_{\text{CO}})] \times 100\%$$

where V_{CO} and V'_{CO} are the inlet and outlet volume fraction of CO, respectively.

The uncertainty of the measured CO conversion is around 5% with 95% confidential interval.

3. Results and discussion

3.1. Physicochemical characterizations of the MgAl-LDHs and MgAl-LDOs

XRD characterization was carried out to identify the structure of as-prepared samples. As shown in Fig. 1, the characteristic diffraction peaks of LDHs with a rhombohedral symmetry (3R) were observed in all samples. The diffraction peaks at $2\theta = 13.7^\circ, 27.4^\circ, 40.7^\circ, 46.5^\circ,$

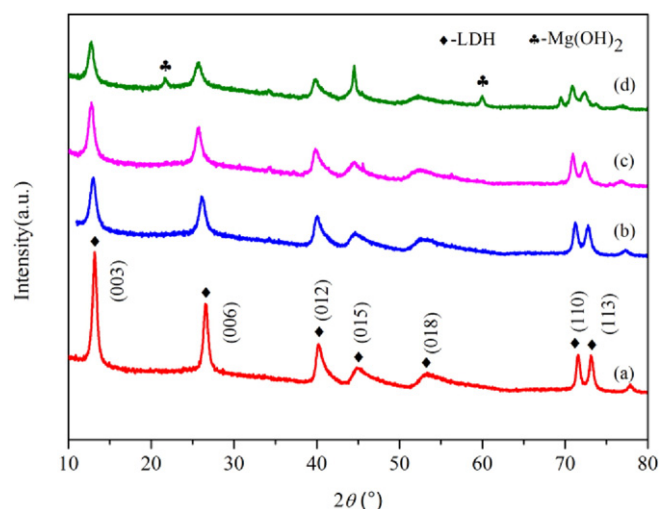


Fig. 1. XRD patterns of the as-prepared MgAl-LDHs precursors with different Mg/Al molar ratios: (a) 3:1, (b) 4:1, (c) 5:1, and (d) 6:1.

$55.4^\circ, 71.9^\circ,$ and 73.6° could be indexed respectively to the (003), (006), (012), (015), (018), (110), and (113) lattice planes of MgAl-LDH (JCPDS No. 00-035-0965). The phases of $\text{Mg}(\text{OH})_2$ was detected as impurity on the sample with Mg/Al = 6, whereas on other samples, no other diffraction peaks of impurities were discerned, indicating that the as-synthesized precursors have a pure LDHs phase.

It is well known that upon thermal treatment, the LDHs firstly lose the interlayer water, and then dehydroxylate and decarbonate (denitrate for the samples in this work) to a large extent, leading to the formation of mixed metal oxides [12]. Fig. 2 shows the XRD patterns of the MgAl-LDOs obtained by calcination of the MgAl-LDHs at 700 °C. Two main reflections at $2\theta = 51.2^\circ$ and 74.9° , accompanied by two small peaks above 90° were observed. These reflection characteristics are very similar to those of MgO [13], thus can be assigned to the Mg(Al)O phase formed by dissolution of Al^{3+} ions into the MgO structure [14,15]. Nevertheless, the co-presence of trace MgAl_2O_4 could not be excluded by XRD due to the similar lattice parameters. With the increase of Mg/Al molar ratio, the intensity of the Mg(Al)O diffraction peaks is increased. Based on the strongest peak at $2\theta = 51.2^\circ$, the average particle size of the Mg(Al)O was calculated by the Scherrer equation and is listed in Table 1. It is found that the average particle size of the Mg(Al)O increases remarkably from 9.44 to 11.02 nm as the Mg/Al

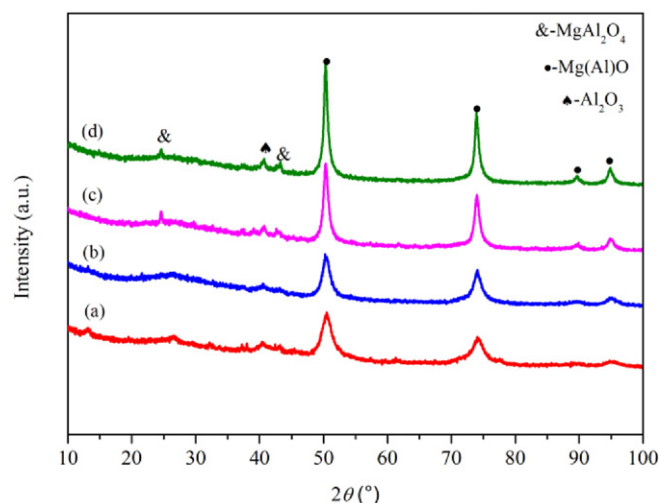


Fig. 2. XRD patterns of the MgAl-LDO support with different Mg/Al molar ratios: (a) 3:1, (b) 4:1, (c) 5:1, and (d) 6:1.

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