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Short communication

Preparation of a highly dispersed Ni_2P/Al_2O_3 catalyst using Ni–Al–CO_3^{2-} layered double hydroxide as a nickel precursor

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ABSTRACT

We now report a novel method for the synthesis of a Ni_2P/Al_2O_3-LW catalyst using Ni–Al–CO_3^{2-} layered double hydroxide (Ni–Al–CO_3^{2-}-LDH) as a nickel precursor and ammonium dihydrogen phosphate as a phosphorous precursor under microwave–hydrothermal (MWH) treatment for 20 min at 363 K. The catalysts were characterized by XRD, TPR, BET, CO uptake and XPS. MWH treatment can promote the formation of smaller and highly dispersed Ni_2P particles and a higher surface area of the catalyst. The Ni_2P/Al_2O_3-LW shows hydrodesulfurization activity of 99.3%, which was much higher than that found for the Ni_2P/Al_2O_3 catalyst obtained via an impregnation method.

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1. Introduction

Recently, hydrodesulfurization (HDS) of fuel oils has received a lot of attention due to more stringent environmental regulations enacted throughout the world. Therefore, the development of highly active HDS catalysts has been an urgent subject worldwide [1–3]. In order to effectively achieve HDS, many efforts have been devoted to prepare excellent active catalysts including phosphide, carbide and nitride catalysts [4,5]. In recent years, catalysts for HDS derived from layered double hydroxide (LDH) precursors have attracted a lot of attention because their HDS activity was much higher than those found for other conventional catalysts [6,7].

LDH is a class of material with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations within the hydrotalcite-like compounds, respectively, and A^{n-} denotes an organic or inorganic anion [8]. The M^{2+} and M^{3+} cations are uniformly dispersed within the layers. Thus, these layered materials have been widely used as catalysts, catalyst precursors or catalyst supports [9]. Li et al. [10] have reported a $NiAl_3MoW$-5 catalyst with a layered structure that showed about two times higher HDS activity than commercially available catalysts. Faro Jr. et al. [11] found that an unsupported NiMoAl catalyst prepared from NiAl-terephthalate LDH showed higher HDS activity than that found for the conventional $NiMo/Al_2O_3$ catalyst. An unsupported CoMgMoAl hydrotreated catalyst prepared from CoMgAl-terephthalate LDH possessed higher HDS selectivity than that found for a commercially available $CoMo/Al_2O_3$ catalyst [12].

Microwave irradiation has been applied for the rapid synthesis of inorganic solids and organic reactions [13]. It was found that hydrotalcites obtained by a microwave–hydrothermal (MWH) method present smaller crystallite sizes with improved dispersion and higher specific surface area than conventional samples [14]. Siffert et al. [15] have prepared a Co–Al mixed oxide catalyst using microwave irradiation, which possessed smaller particle sizes and a larger surface area and showed improved activity than that found for the corresponding catalyst prepared using a co-precipitation method. However, to the best of our knowledge, the Ni_2P catalyst derived from an LDH precursor has not been previously reported for use in HDS.

In this work, the Ni_2P/Al_2O_3-LW catalyst precursor was prepared via a novel method using Ni–Al–CO_3^{2-}-LDH as the nickel precursor and $NH_4H_2PO_4$ as a phosphorous precursor under MWH treatment conditions. The Ni_2P/Al_2O_3-LW catalyst, which exhibits a smaller crystallite size and better dispersion of active Ni_2P particles was obtained after H_2 reduction.

2. Experimental

2.1. Synthesis of Ni–Al–CO_3^{2-}-LDH

The pristine Ni–Al–CO_3^{2-} layered double hydroxide (Ni–Al–CO_3^{2-}-LDH) was prepared by coprecipitation. An aqueous solution of NaOH (0.67 mol/L) and Na_2CO_3 (0.02 mol/L) was added dropwise into a mixed salt solution of $Ni(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ (a Ni^{2+}/Al^{3+} molar ratio of 3/1) up to the pH of 10 under stirring. The resulted

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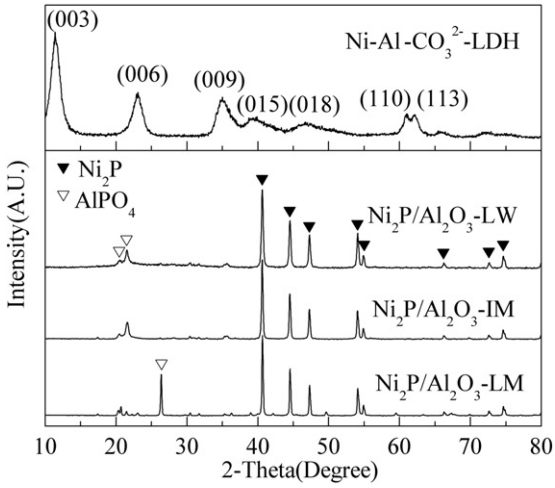

Fig. 1. XRD patterns of the Ni–Al–CO_3^{2-}-LDH and Ni_2P/Al_2O_3-X catalysts.

mixture was aged at 333 K for 6 h. The precipitates were filtered and washed with deionized water to obtain the Ni–Al–CO_3^{2-}-LDH. The Ni–Al–CO_3^{2-}-LDH was calcined to obtain Ni–Al–CO_3^{2-} layered double oxide (denoted as Ni–Al–CO_3^{2-}-LDO).

2.2. Preparation of catalyst precursor

The Ni–Al–CO_3^{2-}-LDH was added into an ammonium dihydrogen phosphate ($NH_4H_2PO_4$) solution and treated using MWH for 20 min at 363 K under reflux. The suspension was dried at 393 K for 10 h to obtain the catalyst precursor of Ni_2P/Al_2O_3-LW.

For comparison, the catalyst precursors were prepared by a standard incipient wetness impregnation of the Ni–Al–CO_3^{2-}-LDH with a $NH_4H_2PO_4$ solution for 24 h and impregnation of Al_2O_3 with a mixture of $NH_4H_2PO_4$ and $Ni(NO_3)_2 \cdot 6H_2O$ solution, respectively. The resulting solids were dried at 393 K for 10 h to obtain the catalyst precursors Ni_2P/Al_2O_3-LM and Ni_2P/Al_2O_3-IM, respectively.

2.3. Synthesis of Ni_2P/Al_2O_3-X catalyst

The obtained precursors of Ni_2P/Al_2O_3-LW, Ni_2P/Al_2O_3-LM and Ni_2P/Al_2O_3-IM were calcined at 773 K for 3 h, and then reduced in a fixed-bed reactor by heating to 973 K at a rate of 2 K min^{-1} in a flow of H_2, held for 2 h, then naturally cooled to room temperature in a continuous H_2 flow. The obtained catalyst was passivated in O_2/N_2 mixture (0.5 vol.% of O_2) with flow rate of 20 mL/min for 2 h to obtain the corresponding Ni_2P/Al_2O_3-X (X = LW, LM, IM) catalysts with Ni loading of 64.4 wt.% and an initial Ni/P molar ratio of 1/2, and then which was subjected to characterization.

2.4. Characterization of catalyst

X-ray diffraction (XRD) analysis was carried out on a D/max-2200PC-X-ray diffractometer. Temperature-programmed reduction (TPR) experiments were carried out with a Builder PCA-1200 apparatus. The specific surfaces (BET) of the catalysts were obtained by using micromeritics adsorption equipment of TRISTAR II 3020. CO chemisorption uptake measurements were performed in a micromeritics ASAP 2010 apparatus. The XPS spectra were acquired using ESCALAB MKII spectrometer. XPS measurements were performed using monochromatic Mg *K*α radiation (E = 1253.6 eV). The recorded photoelectron binding energies were referenced against the C 1s contamination line at 284.8 eV. Transmission electron microscope (TEM) examinations were performed using the JEM-1010 instrument supplied by JEOL.

2.5. Catalytic activities

The HDS of dibenzothiophene (DBT) was performed in a flowing high-pressure fixed bed stainless steel catalytic reactor (6 mm in diameter, and 400 mm in length) using a feed consisting of a decalin solution of DBT (1 wt.%). Catalytic activities were measured at 613 K, 3.0 MPa, weight hourly space velocities (WHSV) of 2.0 h^{-1} and hydrogen/oil ratio of 500 (V/V). The catalysts were pressed in disks, crushed, and sieved with 20–40 mesh before use. Prior to reaction, 0.65 g of the catalysts were pretreated in situ with flowing H_2 (40 mL/min) at 773 K for 2 h. Sampling of liquid products was started 2 h after the steady reaction conditions had been achieved. The liquid samples were collected every hour and analyzed by FID gas chromatography with a GC-14C-60 column.

3. Results and discussion

3.1. XRD

As can be seen in Fig. 1, the reflection of the planes (003), (006), (009), (012), (015) and (018) of crystalline LDH were attributed to Ni–Al–CO_3^{2-}-LDH. Meanwhile, the typical doublet of the d(110)–d(113) planes of LDH can be clearly observed in the zone around 2θ = 60–62°. The XRD pattern for Ni–Al–CO_3^{2-}-LDH was similar to those reported in the literature [9] for LDH phases, showing that Ni–Al–CO_3^{2-}-LDH was successfully prepared.

For all Ni_2P/Al_2O_3-X, the strong diffraction peaks at 2θ = 40.6°, 44.5°, 47.1° and 54.1° (PDF: 03-0953) can be ascribed to the Ni_2P phase, which indicates that the Ni_2P phase was the dominant phase. However, the $AlPO_4$ peaks were observed for all the catalysts, which were caused by the strong interactions found between aluminum and phosphorus [16]. Moreover, when compared to Ni_2P/Al_2O_3-IM and Ni_2P/Al_2O_3-LM, the width of the Ni_2P phase of Ni_2P/Al_2O_3-LW was increased. In general, an increase in peak width of the Ni_2P phase exhibits a decrease in the crystallite size (D_c) of the Ni_2P phase. The D_c calculated from Scherrer's equation is listed in Table 1 [17,18]. It can be seen from TEM analysis (Fig. S1 and S2) that the Ni_2P particle sizes ranged from approximately 13 to 75 nm for Ni_2P/Al_2O_3-LM catalyst and from 13 to 59 nm for Ni_2P/Al_2O_3-IM. The Ni_2P/Al_2O_3-LW possessed the smallest Ni_2P particle sizes, which ranged from approximately 7 to 42 nm with average crystallite size of 28.4 nm. This agreed with the result (28.2 nm) obtained by XRD analysis (column 5 of Table 1). The MWH treatment could suppress agglomeration during the nucleation and crystal growth processes,

Table 1
Textural properties of the Ni–Al–CO_3^{2-}-LDO, Al_2O_3 and Ni_2P/Al_2O_3-X catalysts.

Sample	S_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore size (nm)	D_c[a] (nm)	CO uptake (μmol g^{-1})	Conversion[b] (%)	Selectivity (%)[b]	
							CHB	BP
Ni_2P/Al_2O_3-LW	29.0	0.183	24.7	28.2	227	99.3	24.7	75.3
Ni_2P/Al_2O_3-IM	9.2	0.042	17.7	34.5	176	88.5	35.2	64.8
Ni_2P/Al_2O_3-LM	5.1	0.001	9.0	40.7	59	55.5	21.5	78.5
Ni–Al–CO_3^{2-}-LDO	87.0	0.220	9.9	–	–	–	–	–
Al_2O_3	255.5	0.314	4.9	–	–	–	–	–

[a] Calculated from the $D_c = K\lambda/\beta \cos(\theta)$ (Scherrer equation) based on the Ni_2P {1 1 1}.
[b] Reaction conditions: T = 653 K, P = 3.0 MPa, WHSV = 2.0 h^{-1}, H_2/oil (V/V) = 500.

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