



Short communication

Microwave-assisted hydrothermal synthesis of NiS_x and their promotional effect for the hydrodeoxygenation of *p*-cresol on MoS₂



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ABSTRACT

NiS_x were synthesized by microwave assisted hydrothermal method using nickel nitrate and thiourea as precursor materials. Their phase compositions were controlled by adjusting the reaction temperature and pH value. In the hydrodeoxygenation (HDO) of *p*-cresol on MoS₂, adding NiS_x enhanced the conversion but had no effect on the product distribution. NiS₂ phase exhibited higher promotional effect than NiS and Ni₃S₄ phases. The HDO reaction mechanism for *p*-cresol on NiS_x + MoS₂ could be well explained by the Remote Control model through a migration of spillover hydrogen.

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1. Introduction

MoS₂ had been widely studied in the HDO of oxygen-containing compounds from bio-oil and exhibited high activity [1–4] and its activity was enhanced by adding promoter Ni [5–8]. There had developed two main models to explain the synergetic effect between Ni and Mo in Ni–Mo bimetallic sulfide: Co–Mo–S model and Remote Control model [9,10]. The former had reasonably illuminated the promotional effect of Ni for MoS₂ activity by the formation of Ni–Mo–S phase in the homogeneous simultaneous precipitation procedure [5], but Ni–Mo–S phase was hard to directly detect and was unstable at high temperature [11]. The latter had proposed and evidenced that the synergistic effect between NiS_x and MoS₂ was explained through a migration of spillover hydrogen, where the spillover hydrogen was generated on donor (NiS_x) and migrated to the active phase of acceptor (MoS₂) [12–16]. However, until now, several Ni sulfide phases such as Ni₃S₄ [5], NiS₂ [17], NiS [18] and Ni₇S₆ [19] had been detected in Ni–Mo sulfide catalysts, but which phase, possessing the highest catalytic activity, was still unclear.

Various methods had been developed to synthesize NiS_x in the previous literatures [20–22]. Normal hydrothermal synthesis had been one of the interesting methods for the controllable synthesis of NiS_x

with different phases and morphologies [23], but this approach was rather slow and inefficient, and had to take a long time [24]. Recently, microwave-assisted hydrothermal method had been successfully applied into the synthesis of metal sulfides because microwave offered a rapid initial heating, faster kinetics and homogeneous thermal transmission, which significantly reduced the reaction time and easy controlled phase composition and morphology [25,26]. Therefore, we adopted the advantages of microwave-assisted hydrothermal method and changed the reaction temperature and pH value of the reaction system to synthesize NiS_x with different phase compositions using Ni(NO₃)₂ and H₂NCSNH₂ as raw materials. The promotional effects of the NiS_x phase compositions on the catalytic activity of MoS₂ were studied taking the HDO of *p*-cresol as a probe.

2. Experimental

2.1. Synthesis of samples

In a typical experiment, 6 mmol nickel nitrate and 30 mmol thiourea were dissolved in 30 mL ultra-pure water, and then hydrochloric acid was added into the above solution to adjust its pH value to 0.8. After treating the mixed solution at 200 °C for 2 h under microwave irradiation, the resultant product were separated and washed with absolute ethanol several times. Finally, the samples were dried under vacuum at 50 °C for 5 h and then stored in nitrogen. Different samples were synthesized by changing the reaction temperature and pH value and their names were listed in Table 1. MoS₂ was prepared by the same

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Table 1
Phase compositions of NiS_x prepared at different pH values and temperatures.

Sample	pH value	Temperature (°C)	Phase composition (wt.%)		
			NiS	Ni ₃ S ₄	NiS ₂
Ni-S-1	0.8	160	24.5	0	75.5
Ni-S-2	0.8	180	20.0	5.4	74.6
Ni-S-3	0.8	200	0	0	100
Ni-S-4	1.4	200	11.7	25.0	63.3
Ni-S-5	1.4	200	11.6	7.8	80.6
Ni-S-6	0.9	200	0	9.2	90.8
Ni-S-7	0.7	200	0	3.0	97.0

method as that in our previous study [27], where the reaction temperature, time, pressure and pH value was 200 °C, 12 h, 1.5 MPa and 0.9, respectively.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried on a D/max2550 18KW Rotating anode X-Ray Diffractometer with monochromatic Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) radiation at voltage and current of 40 kV and 300 mA. The 2θ was scanned over the range of 5–90° at a rate of 10°/min. The morphology of samples was characterized by scanning electronic microscopy (SEM) on a JEOL JSM-6360 electron microscopy.

2.3. Activity measurement

The catalytic activity measurements were carried out in a 100-mL sealed autoclave. NiS_x (0.01 g), MoS₂ (0.03 g) with a surface area of 170 m²/g, *p*-cresol (1.50 g) and dodecane (15.00 g) were placed into the autoclave. Air in the autoclave was evacuated by pressurization–depressurization cycles with nitrogen and subsequently with hydrogen. The system was heated to 300 °C, then pressurized with hydrogen to 4.0 MPa and adjusted the stirring speed to 900 rpm. After 5 h, liquid sample was withdrawn from the reactor and analyzed by Agilent 6890/5973 N GC–MS and 7890 gas chromatography using a flame ionization detector with a 30 m AT–5 capillary column. The synergism factor (SF) was used to describe the promotional effect of NiS_x and calculated by the conversion on NiS_x and MoS₂/the conversion only on MoS₂.

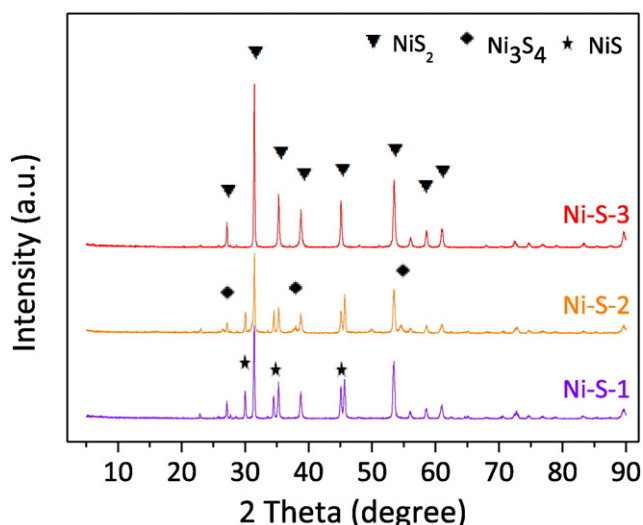


Fig. 1. XRD patterns of NiS_x prepared at different temperatures.

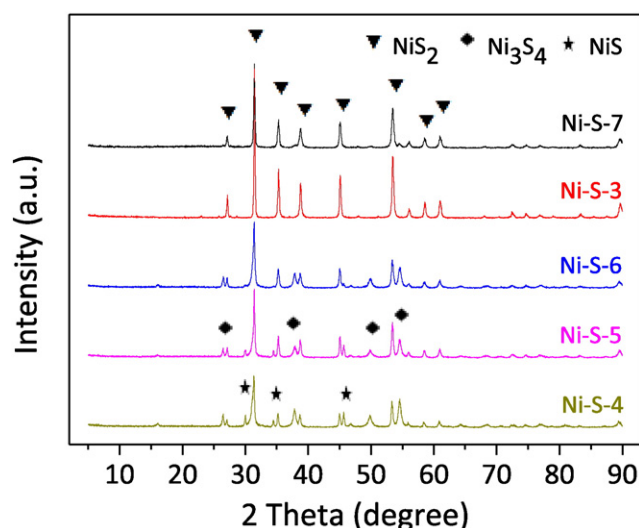


Fig. 2. XRD patterns of NiS_x prepared at different pH values.

3. Results and discussion

3.1. Effect of reaction temperature

Because reaction temperature was one of important roles for the phase control synthesis of materials [28], NiS_x samples were prepared at different temperatures and characterized by XRD to determine their structures firstly. As shown in Fig. 1, some sharp diffraction peaks at $2\theta = 27.1^\circ, 31.5^\circ, 35.3^\circ, 38.8^\circ, 45.1^\circ, 53.5^\circ, 56.1^\circ, 58.6^\circ$ and 61.0° matched well with cubic NiS₂ (JCPDS No. 01–088–1709) [20]. For Ni-S-1, beside the peaks to cubic NiS₂, there also presented three sharp peaks at $2\theta = 30.0^\circ, 34.5^\circ$ and 45.6° , corresponding to NiS [29,30]. Several small peaks appeared at $2\theta = 26.4^\circ, 37.9^\circ, 49.9^\circ$ and 54.4° in the XRD pattern of Ni-S-2, attributing to Ni₃S₄ [31,32]. The XRD pattern of Ni-S-3 presented no peak to NiS and Ni₃S₄, all peaks were attributed to NiS₂.

The phase composition of the samples prepared at different temperatures were calculated by the XRD–K value method as reported in previous literatures [33,34] and the results are summarized in Table 1. Ni-S-1 was composed by 24.5% NiS and 75.5% NiS₂. When the temperature was increased to 180 °C, NiS₂ and NiS phase contents decreased by 0.9% and 4.5%, respectively, but Ni₃S₄ phase was observed, accounting for 5.4%. At 200 °C, NiS₂ phase content increased to 100%. These phase

Table 2

The conversion, products distribution and synergism factor in the HDO of *p*-cresol on NiS_x + MoS₂ at 300 °C for 5 h.

Catalyst	Conversion (mol%)	Product distribution (mol%) ^a			SF
		3-MCHE	MCH	TOL	
Ni-S-1 ^b	6.8	1.9	11.0	87.1	–
Ni-S-3 ^b	12.2	2.3	11.2	86.5	–
Ni-S-5 ^b	8.1	2.2	11.2	86.6	–
MoS ₂ ^b	43.1	5.6	10.6	83.8	1.00
Ni-S-1 + MoS ₂ ^c	59.2	4.5	10.9	84.6	1.37
Ni-S-2 + MoS ₂ ^c	57.9	4.3	10.2	85.5	1.34
Ni-S-3 + MoS ₂ ^c	72.8	4.0	11.5	84.5	1.69
Ni-S-4 + MoS ₂ ^c	52.6	4.0	9.5	86.5	1.22
Ni-S-5 + MoS ₂ ^c	59.6	4.8	11.8	83.4	1.38
Ni-S-6 + MoS ₂ ^c	63.8	3.4	8.6	88.0	1.48
Ni-S-7 + MoS ₂ ^c	62.4	4.5	11.7	83.8	1.59

^a Products: 3-MCHE = 3-methylcyclohexene, MCH = methylcyclohexane, TOL = toluene.

^b Catalyst weight was 0.03 g.

^c Catalyst was 0.01 g Ni-S-X and 0.03 g MoS₂.

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