Accepted Manuscript

Microwave-assisted hydrothermal synthesis of NiS_x and their promotional effect for the hydrodeoxygenation of *p*-cresol on MoS $_2$

Weiyan Wang, Kui Wu, Lu Li, Song Tan, Guohua Zhu, Wensong Li, Zhiqiang He, Yunquan Yang

 PII:
 S1566-7367(15)30127-8

 DOI:
 doi: 10.1016/j.catcom.2015.10.032

 Reference:
 CATCOM 4490

To appear in: Catalysis Communications

Received date:26 August 2015Revised date:18 October 2015Accepted date:27 October 2015

Please cite this article as: Weiyan Wang, Kui Wu, Lu Li, Song Tan, Guohua Zhu, Wensong Li, Zhiqiang He, Yunquan Yang, Microwave-assisted hydrothermal synthesis of NiS_x and their promotional effect for the hydrodeoxygenation of p-cresol on MoS₂, *Catalysis Communications* (2015), doi: 10.1016/j.catcom.2015.10.032

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Microwave-assisted hydrothermal synthesis of NiS_x and their promotional effect for the hydrodeoxygenation of *p*-cresol on MoS_2

Weiyan Wang^{a, b}*, Kui Wu^a, Lu Li^a, Song Tan^a, Guohua Zhu^a, Wensong Li^a, Zhiqiang He^a, Yunquan Yang^{a, b}*

^a School of Chemical Engineering, Xiangtan University, Xiangtan, Hunan, 411105, PR

China

^b National & Local United Engineering Research Centre for Chemical Process Simulation and Intensification, Xiangtan University, Xiangtan 411105, P. R. China

* To whom correspondence should be addressed.

E-mail: wangweiyan@xtu.edu.cn (W. Wang), yangyunquan@xtu.edu.cn (Y. Yang)

Tel: (+86) 731-58298581

Fax: (+86) 731–58293284

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.

Keyword: NiS_{*x*}; Phase composition; Microwave-assisted hydrothermal method; Hydrodeoxygenation; MoS_2 ; Remote Control model

1. Introduction

 MoS_2 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 sulphide: Co–Mo–S model and remote control model [9, 10]. The former had reasonably illuminated the promotional effect of Ni for MoS_2 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 sulphide phases such as Ni₃S₄ [5], NiS₂ [17], NiS [18] and Ni₇S₆ [19] had been detected in Ni–Mo sulphide 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 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 $Ni(NO_3)_2$ and H_2NCSNH_2 as raw materials. The promotional effects of the NiS_x phase compositions on the catalytic activity of MoS_2 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 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 hours 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. MoS_2 was prepared by the same 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 (λ =1.5418 Å) radiation at voltage and current of 40 kV and 300 mA. The 2 θ was scanned over the range of 5–90° at a rate of 10°/min. The morphology of samples were 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 6890/5973N 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.

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 θ = 27.1°, 31.5°, 35.3°, 38.8°, 45.1°, 53.5°, 56.1°, 58.6° 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 θ = 30.0°, 34.5° and 45.6°, corresponding to NiS [29, 30]. Several small peaks appeared at 2 θ = 26.4°, 37.9°, 49.9° 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 compositions changes were related to the decomposition of thiourea. It was well known that thiourea decomposed to H₂S, NH₃ and CO₂ in the water. At higher temperature, its decomposition rate was enhanced, which supplied sufficient S^{2–} for the formation of NiS₂. In contrast, there formed other phases with low S/Ni atom ratio, such as NiS (1:1) and Ni₃S₄ (4:3).

3.2 Effect of pH values in raw material solution

Fig. 2 shows the XRD patterns of NiS_x samples prepared under the different pH values. With the decrement of pH value, the intensity of the peaks to NiS and Ni₃S₄ weakened while the peak intensity for NiS₂ strengthen. Except for NiS₂ cubic phase, no other phase was observed when the pH value was decreased to 0.8. The peak intensity for NiS₂ in the XRD pattern of Ni–S–7 decreased and there appeared some small peaks to Ni₃S₄. As listed in table 2, Ni–S–4 was composed by 11.7% NiS, 25.0% Ni₃S₄ and 63.3% NiS₂. Because the decomposition of thiourea was enhanced and produced much H₂S at low pH value, the required H₂S for the formation of NiS₂ became adequate, leading to the increase of NiS₂ phase content in the sample. However, at the same time, the production rate of NH₃ was also raised, which increased the pH value of the reaction system. Therefore, some other phases with low S/Ni atom ratio would produce when the pH

value was decreased excessively. As shown in the XRD pattern Ni–S–7, there appeared 3.0% Ni₃S₄ phase in the sample.

The SEM characterization results also evidenced the phase change phenomenon. As shown in Fig. 3, Ni–S–3 displayed cube–like particles without any other irregular particles. Assisted with the XRD results, this cube–like particles were attributed NiS₂. Ni–S–4, Ni–S–5 and Ni–S–6 samples presented not only small cubic particles but also large irregular particles, corresponding to NiS₂ phase and other phases, respectively. The SEM image of Ni–S–7 showed some cubic particles with a size range of 3–8 μ m, presenting an increase tendency on the particle size with the further decrement of pH value.

3.3 Promotional effect of NiS_x in the HDO of p-cresol on MoS_2

To determine the catalytic activity of NiS_x samples with different phase compositions, Ni–S–1, Ni–S–3 and Ni–S–5 were selected as catalysts for the HDO of *p*–cresol firstly. As shown in Table 3, Ni–S–3 showed the highest HDO activity among these three samples, but the conversion on this catalyst was only 12.2% with a selectivity of 86.5% toluene after reaction at 300 °C for 5 h, exhibiting its very low HDO activity. Fortunately, Gil–Llambías et al. [12] and A. N. Varakin et al. [15] had evidenced the synergetic effect between NiS_x/CoS_x and MoS₂. Hence, the prepared samples were selected to investigate the effect of phase composition of NiS_x on the conversion and product distribution in the HDO of *p*–cresol on MoS₂. In these HDO processes, the weight of NiS_x was reduced to 0.01 g, the HDO conversion on 0.01 g NiS_x would be much lower than that on 0.03 g NiS_x. The conversion and toluene selectivity in the HDO of *p*–cresol on MoS₂ without

adding NiS_x was 43.1% and 83.8%, respectively. At the presence of NiS_x, the conversion was increased, but it had no obvious effect on the product distribution. Generally, the HDO of *p*-cresol followed two parallel routes: direct deoxygenation (DDO) via aromatic C–O bond scission and hydrogenation-dehydration (HYD) via saturation of aromatic ring [35], as shown in Scheme 1. 4-Methylcyclohexanol and 4-methylcyclohexanone were intermediates for the formation of methylcyclohexane, but were not detected in the products, indicating their high reactivity on the tested catalysts under the studied conditions [36]. Previous studies had also reported these similar results on sulfide catalysts [1, 17, 37].

In this study, NiS_x and MoS₂ were added separately, and there was impossible to form a mixture phase (Ni–Mo–S). According to the Remote Control model [12, 14], spillover hydrogen (H_{so}) generated on NiS_x phase and then migrated to MoS₂ for HDO reaction, which enhanced the conversion in the HDO of *p*–cresol. The very low conversion on NiS_x and the two separated reaction routes on NiS_x+MoS₂ showed that *p*–cresol was mainly adsorbed on MoS₂ active site via two ways: vertical adsorption through the oxygen atom and co-plane adsorption through the aromatic ring firstly, and then H_{so} attacked the C_{aromatic}–O bond or π bond of benzene ring for the HDO reaction. Table 2 showed that the SF in the HDO of *p*–cresol decreased with the order of Ni–S–3+MoS₂ (1.69) > Ni–S–7+MoS₂ (1.59) > Ni–S–6+MoS₂ (1.48) > Ni–S–5+MoS₂ (1.38) > Ni–S–1+MoS₂ (1.37) > Ni–S–2+MoS₂ (1.34) > Ni–S–4+MoS₂ (1.22). This change trend was well consistent with the NiS₂ phase content in NiS_x samples, suggesting a better promotional effect of NiS₂ phase for the HDO activity of MoS₂ than NiS and Ni₃S₄

phases, which might result from the more coordinatively unsaturated sites in NiS₂ due to its higher S/Ni ratio [38]. When the pH value was decreased from 0.8 to 0.7, although NiS₂ phase content in Ni–S–7 was high to 97.0%, the cube–like particle size increased, leading to a decrease of the created spillover hydrogen and a reduction on the conversion.

4. Conclusion

NiS_x samples with different phase compositions were synthesized by microwave assisted hydrothermal method. The reaction temperature and pH value of the mixed solution had great effects on the phase composition. In the HDO of *p*–cresol, the prepared NiS_x showed low HDO activity but exhibited good synergetic effect with MoS₂. The presence of NiS_x enhanced *p*–cresol conversion, but had no obvious effect on the product distribution. According to the Remote Control model, *p*–cresol molecules were mainly adsorbed on MoS₂ active sites firstly, and then H_{so} created on the NiS_x and migrated to MoS₂ sites to attack the C_{aromatic}–O bond or benzene ring π bond for the HDO reaction. The activity tests presented that NiS₂ phase exhibited better promotional effect than NiS and Ni₃S₄ phases and the SF reached to 1.69. This study was beneficial to the design and preparation Ni–Mo bimetallic sulphide catalysts with high HDO activity.

Acknowledgment

This research was supported by the National Natural Science Foundation of China (No. 21306159, 21376202), Scientific Research Fund of Hunan Provincial Education Department (15B234) and Students' innovation and entrepreneurship training program of Hunan Province (2015xtusj011).

Reference

- [1] V. Itthibenchapong, C. Ratanatawanate, M. Oura, K. Faungnawakij, Catal. Commun.68 (2015) 31-35.
- [2] G. Veryasov, M. Grilc, B. Likozar, A. Jesih, Catal. Commun. 46 (2014) 183-186.
- [3] P.E. Ruiz, B.G. Frederick, W.J. De Sisto, R.N. Austin, L.R. Radovic, K. Leiva, R. García, N. Escalona, M.C. Wheeler, Catal. Commun. 27 (2012) 44-48.
- [4] M. Grilc, G. Veryasov, B. Likozar, A. Jesih, J. Levec, Appl. Catal. B: Environ. 163 (2015) 467-477.
- [5] B. Yoosuk, D. Tumnantong, P. Prasassarakich, Fuel 91 (2012) 246-252.
- [6] W. Wang, L. Li, K. Wu, K. Zhang, J. Jie, Y. Yang, Appl. Catal. A: Gen. 495 (2015)8-16.
- [7] A. Srifa, N. Viriya-empikul, S. Assabumrungrat, K. Faungnawakij, Catal. Sci. Technol. 5 (2015) 3693-3705.
- [8] M. Grilc, B. Likozar, J. Levec, Appl. Catal. B: Environ. 150–151 (2014) 275-287.
- [9] J. Ojeda, N. Escalona, P. Baeza, M. Escudey, F.J. Gil-Llambias, Chem. Commun. (2003) 1608-1609.
- [10] H. Topsøe, B.S. Clausen, Catal. Rev. 26 (1984) 395-420.
- [11] P. Grange, X. Vanhaeren, Catal. Today 36 (1997) 375-391.
- [12] P. Baeza, M.S. Ureta-Zañartu, N. Escalona, J. Ojeda, F.J. Gil-Llambías, B. Delmon, Appl. Catal. A: Gen. 274 (2004) 303-309.
- [13] N. Escalona, R. García, G. Lagos, C. Navarrete, P. Baeza, F.J. Gil-Llambías, Catal.Commun. 7 (2006) 1053-1056.
- [14] R. Prins, Chem. Rev. 112 (2012) 2714-2738.

- [15] A.N. Varakin, P.A. Nikul'shin, A.A. Pimerzin, V.A. Sal'nikov, A.A. Pimerzin, Russ.
- J. Appl. Chem. 86 (2013) 718-726.
- [16] A.A. Pimerzin, P.A. Nikulshin, A.V. Mozhaev, A.A. Pimerzin, A.I. Lyashenko, Appl.
- Catal. B: Environ. 168–169 (2015) 396-407.
- [17] C. Wang, Z. Wu, C. Tang, L. Li, D. Wang, Catal. Commun. 32 (2013) 76-80.
- [18] J. Bocarando, R. Huirache-Acuña, W. Bensch, Z.D. Huang, V. Petranovskii, S. Fuentes, G. Alonso-Núñez, Appl. Catal. A: Gen. 363 (2009) 45-51.
- [19] L. Wang, Y. Zhang, Y. Zhang, Z. Jiang, C. Li, Chem. Eur. J. 15 (2009) 12571-12575.
- [20] G. An, L. Chenguang, Y. Hou, X. Zhang, Y. Liu, Mater. Lett. 62 (2008) 2643-2646.
- [21] S.-L. Yang, H.-B. Yao, M.-R. Gao, S.-H. Yu, CrystEngComm 11 (2009) 1383-1390.
- [22] S. Chen, K. Zeng, H. Li, F. Li, J. Solid State Chem. 184 (2011) 1989-1996.
- [23] M.-R. Gao, Y.-F. Xu, J. Jiang, S.-H. Yu, Chem. Soc. Rev. 42 (2013) 2986-3017.
- [24] L. Wang, Y. Zhu, H. Li, Q. Li, Y. Qian, J. Solid State Chem. 183 (2010) 223-227.
- [25] H. Pang, C. Wei, X. Li, G. Li, Y. Ma, S. Li, J. Chen, J. Zhang, Sci. Rep. 4 (2014) 3577.
- [26] S. Amaresh, K. Karthikeyan, I.C. Jang, Y.S. Lee, J. Mater. Chem. A 2 (2014)11099-11106.
- [27] W. Wang, L. Li, K. Wu, G. Zhu, S. Tan, W. Li, Y. Yang, RSC Adv. 5 (2015)61799-61807.
- [28] W. Dong, X. Wang, B. Li, L. Wang, B. Chen, C. Li, X. Li, T. Zhang, Z. Shi, Dalton Trans. 40 (2011) 243-248.

- [29] A. Ghezelbash, M.B. Sigman, B.A. Korgel, Nano Lett. 4 (2004) 537-542.
- [30] R. Karthikeyan, M. Navaneethan, J. Archana, D. Thangaraju, M. Arivanandhan, Y.
- Hayakawa, Dalton Trans. 43 (2014) 17445-17452.
- [31] N. Mahmood, C. Zhang, Y. Hou, Small 9 (2013) 1321-1328.
- [32] Q. Liu, A. Diaz, A. Prosvirin, Z. Luo, J.D. Batteas, Nanoscale 6 (2014) 8935-8942.
- [33] M. Yan, F. Chen, J. Zhang, M. Anpo, J. Phys. Chem. A 109 (2005) 8673-8678.
- [34] H. Cheng, J. Wang, Y. Zhao, X. Han, RSC Adv. 4 (2014) 47031-47038.
- [35] M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B.C. Gates, M.R.Rahimpour, Energy Environ. Sci. 7 (2014) 103-129.
- [36] O.I. Şenol, E.M. Ryymin, T.R. Viljava, A.O.I. Krause, J. Mol. Catal. A: Chem. 277(2007) 107-112.
- [37] Y.Q. Yang, C.T. Tye, K.J. Smith, Catal. Commun. 9 (2008) 1364-1368.
- [38] A. Olivas, J. Cruz-Reyes, V. Petranovskii, M. Avalos, S. Fuentes, J. Vac. Sci. Technol. A 16 (1998) 3515-3520.



Fig. 1 XRD patterns of NiS_x prepared at different temperatures



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



Fig. 3 SEM images of NiS_x prepared at different pH values



Scheme 1 Proposed reaction routes in the HDO of *p*-cresol on NiS_x+MoS_2

SCR W

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	

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

K K K

				K	
Catalyst	Conversion (mol %)	Product distri	<u>SE</u>		
Cataryst		3-MCHE	МСН	TOL	- 21
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	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

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.

^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.

Graphical abstract

 NiS_x with different phase compositions were synthesized by microwave assisted hydrothermal method. In the HDO of *p*-cresol on MoS₂, the presence of NiS_x enhanced the conversion, but had no obvious effect on the product distribution. The HDO reaction mechanism for *p*-cresol on NiS_x+MoS₂ could be well explained with the Remote Control model through the spillover hydrogen generated on the NiS_x. NiS₂ exhibited better promotional effect for the HDO activity of MoS₂ than NiS and Ni₃S₄.



Highlights

> NiS_x with different phase compositions were synthesized by the microwave-assisted hydrothermal method.

> The phase composition of NiS_x was controlled by adjusting the synthesis conditions.

> The presence of NiS_2 enhanced *p*-cresol conversion but had no effect on product distribution.

> The HDO reaction mechanism could be explained with Remote Control model through the spillover hydrogen.

> NiS₂ exhibited better promotional effect for the HDO activity of MoS_2 than NiS and Ni₃S₄.