Received: 23 November 2017 | Revised: 8 January 2018 | Accepted: 9 January 2018

DOI: 10.1002/aoc.4306

FULL PAPER

WILEY Applied Organometallic Chemistry

A novel route for synthesis of $NiCoP/SiO_2$ hydrodesulfurization catalysts with active S species

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Funding information

National Natural Science Foundation of China, Grant/Award Number: 21103122

We report a new route for synthesis of $NiCoP/SiO_2$ with active S species using NiS and CoS as precursors. The as-prepared catalysts were characterized using X-ray powder diffraction, N_2-adsorption specific surface area measurements, inductively coupled plasma atomic emission spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy (XPS). The catalyst was highly active during the dibenzothiophene hydrodesulfurization (HDS) of $NiCoP/SiO_2$. The XPS spectra of the as-obtained samples show that the surface of NiCoP contains a small amount of S species, which may be responsible for the higher HDS activity.

KEYWORDS

hydrodesulfurization, metal sulfide, nickel cobalt phosphide, red phosphor, S species

1 | INTRODUCTION

Crude oil contains a small amount of sulfides, which are mainly heterocyclic and non-heterocyclic organic sulfides. The combustion of these sulfides produces gaseous sulfur dioxide, which will seriously pollute the environment and damage human health. [1] Therefore, the removal of sulfur compounds from crude oil is imperative. One important solution to this problem is the development of new efficient desulfurization catalysts. The traditional desulfurization catalysts in the industry are mainly cobalt-molybdenum sulfides.[2] Carbides and nitrides have been used to improve the desulfurization efficiency,[3,4] but they will be very easily inactivated owing to the poor sulfur resistance, which severely limits their use. Metal phosphides are a class of desulfurization catalysts discovered recently,[5] including Ni_2P,[6,7] CoP,[8,9] FeP,[10] MoP,[11] NiCoP,[12] NiMoP,[13] and NiFeP.[14] They have high sulfur resistance and desulfurization performance. According to the precious report,[15] metal phosphides treated by H_2S/H_2 are more active than those reduced by H_2, which makes it reasonable to introduce the active phase MPxSy onto the surface of metal phosphides. The activation method is more likely to obtain a small amount of sulfur-containing MPxSy with desulfurization ability. Thus, new methods for synthesis of metal phosphates with active S-containing MPxSy are needed to enhance the performance of metal phosphides. In this paper, NiS and CoS were simultaneously reduced by red phosphor at 700 °C for 15 min to form $NiCoP/SiO_2$ catalysts. The resulting H_2S can react with NiCoP during the preparation of $NiCoP/SiO_2$ to generate an active M-P-S

(M: Ni or Co) phase, which may improve the desulfurization ability of NiCoP/SiO_2 catalyst.[16] Therefore, the preparation route may provide a new method for synthesis of bimetal phosphides with high hydrodesulfurization (HDS) ability.

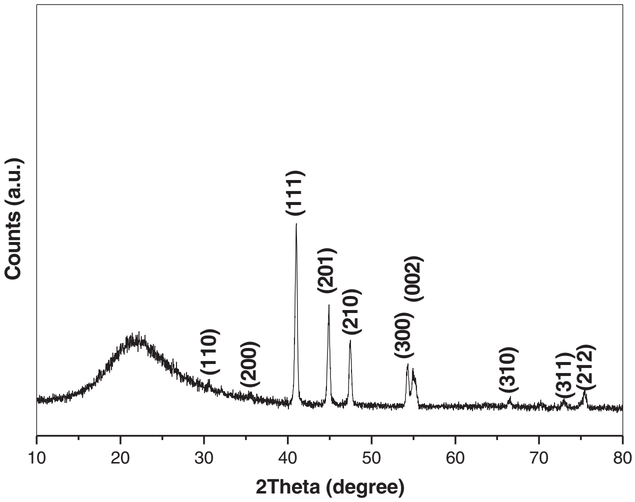

FIGURE 1 X-ray diffraction patterns of NiCoP/SiO_2 (Ni: 10 wt.%, Co: 10 wt.%) obtained at 700 °C for 15 min

2 | EXPERIMENTAL

2.1 | Synthesis of samples

The NiS+CoS/SiO_2 precursor was synthesized as follows: 1.229 g of $NiCl_2{\cdot}6H_2O$ and 1.229 g of $CoCl_2{\cdot}6H_2O$ were dissolved in 15 ml of deionized water separately. Then 2.07 g of SiO_2 (58 m^2/g, 15 nm) was dipped into the mixture of two solutions. The resulting mixture was stirred for 3 h, and then added with 1.23 g of $Na_2S{\cdot}9H_2O$, followed by stirring for 3 h. The NiS+CoS/SiO_2 precursor was filtrated, washed and dried at 120 °C for 6 h. The NiCoP/SiO_2 (Ni: 10 wt.%, Co: 10 wt.%) was synthesized as follows: 1.68 g of the NiS+CoS/SiO_2 precursor and 0.18 g of red P were mixed at the molar ratio of Ni/Co/P = 1:1:6. The mixture was heated to 700 °C under an H_2 atmosphere and aged for 15 min. The furnace was cooled to room temperature. The products were washed and dried at 80 °C for 6 h. Finally, the samples were ground to 20-40 mesh particles.

2.2 | Characterization of samples

X-ray diffraction (XRD) patterns were obtained with a Rigaku D/max 2500 XRD meter using Cu-Kα radiation.

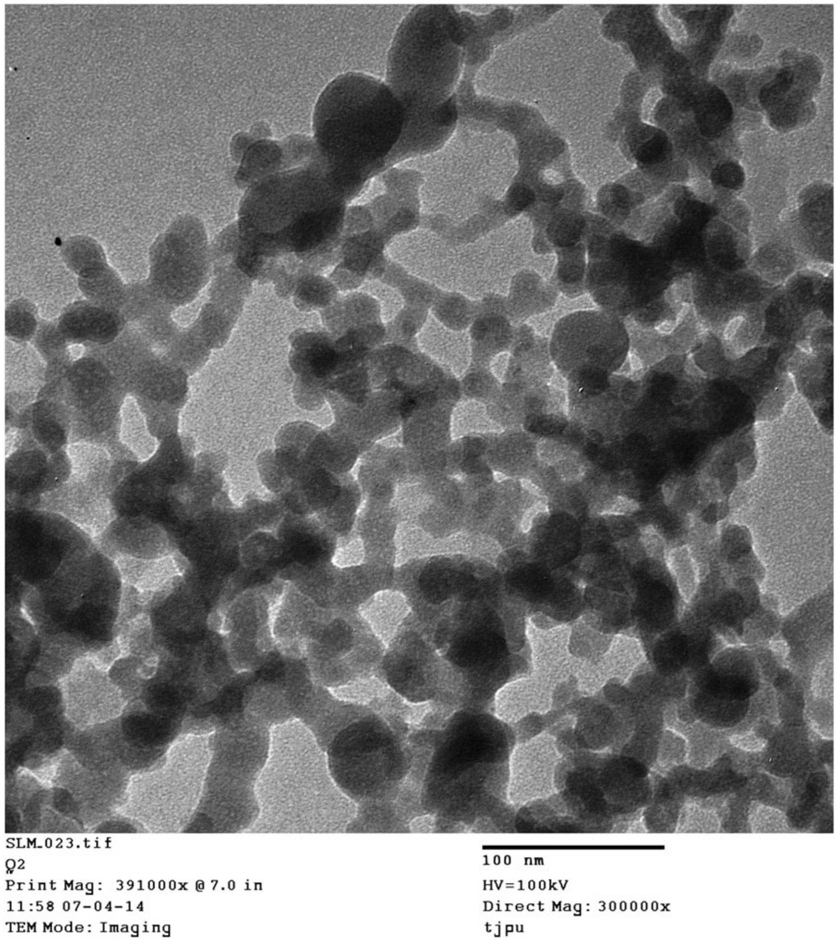

FIGURE 2 TEM image of NiCoP/SiO_2 (Ni: 10 wt.%, Co: 10 wt.%) obtained at 700 °C for 15 min

Specific surface areas of Brunauer-Emmett-Teller (BET) were measured using a Micromeritics ASAP 2020 M apparatus at -196 °C liquid nitrogen temperature. Transmission electron microscopy (TEM) images were obtained on a Hitachi H7650 instrument. The elements were analyzed using a Varian 715-ES inductively coupled plasma atomic emission spectroscope (ICP-AES). Thermogravimetric analysis (TG) of samples was studied on a PerkinElmer simultaneous thermal analyzer (N_2, 15 °C/min). The products of HDS were studied on an Agilent 7890A/5975C gas chromatograph-mass spectrometer (GC-MS).

2.3 | Activity measurement

The HDS of dibenzothiophene (DBT) was conducted in a fixed-bed continuous-flow reactor. About 1 ml of 20–40 mesh NiCoP/SiO_2 (Ni: 10 wt.%, Co: 10 wt.%) was diluted with 4.0 ml of 20-40 mesh SiC and was loaded into the reactor. The reaction conditions were set as follows: total pressure = 3.0 MPa, temperature = 320 °C, 0.5 wt.% DBT in decalin, and H_2 flow = 200 ml/min. The weight hourly space velocity (WHSV) of the feed solution was 9 h^{-1}, and the NiCoP/SiO_2 catalyst was reduced at 400 °C for 3 h in a 200 ml/min H_2 flow. The products were identified off-line by gas chromatography with an OV101 column and a flame ionization detector (FID).

3 | RESULTS AND DISCUSSION

3.1 | Characterization of catalysts

Figure 1 displays the XRD patterns of the as-prepared NiCoP/SiO_2 (Ni and Co both 10 wt.%). The broad diffusion peak at 22° is assigned to the support SiO_2, since the amorphism of SiO_2 provides information about the diffusion peak. All observed peaks except the peak of SiO_2 can be indexed to the pure hexagonal phase of NiCoP (JCPDS cards: no. 71-2336, space group: $P\bar{6}2m$[189]). The sharp and strong peaks from the as-prepared NiCoP suggest high crystallinity in our experimental condition, which helps to improve the catalytic activity. No peak of any other phase (NixPy or CoxPy) was found in Figure 1 . These results indicate that the catalyst NiCoP/SiO_2 was successfully prepared under our experiment conditions. The positions of peaks (210), (300), (002), and (310) of NiCoP slightly shifted to lower angles compared with JCPDS cards. Such non-regular shift may be caused by the instrument.

Typical low-magnification transmission electron microscopy (TEM) image of the as-synthesized NiCoP/SiO_2 (Ni and Co both 10 wt.%) is exhibited in Figure 2. The small gray particles are SiO_2 and the large black particles are NiCoP (Figure 2). The SiO_2 particles in diameter of 15 nm are in a clear catenarian structure. The high surface energy of nanoscale SiO_2 can result in a chain structure. The NiCoP particles in diameter of 20-50 nm are well dispersed on SiO_2 (Figure 2), which may help to enhance their catalytic activity because good dispersion can improve and expose more specific surface area.

The thermal behavior of the mixture of NiS+CoS/SiO_2 precursor and red P (Ni/Co/P molar ratio = 1:1:6) was investigated by thermal gravimetry (TG), derivative TG (DTG) and differential thermal analysis (DTA) (Figure 3). The TG and DTG curves (Figure 3a) exhibit three obvious weight losses with maxima located at 81, 494.7 and 528.7 °C, respectively. The weight loss at 81 °C suggests that the water adsorbed on the sample's surface starts to absorb heat and evaporate at this temperature. The DTA curve (Figure 3b) shows one endothermic peak with a maximum located at 86.7 °C and two exothermic peaks with maxima located at 470.4 and 508 °C. The temperature ranges of the three peaks in the DTA curve correspond well to those of weight losses in the TG and

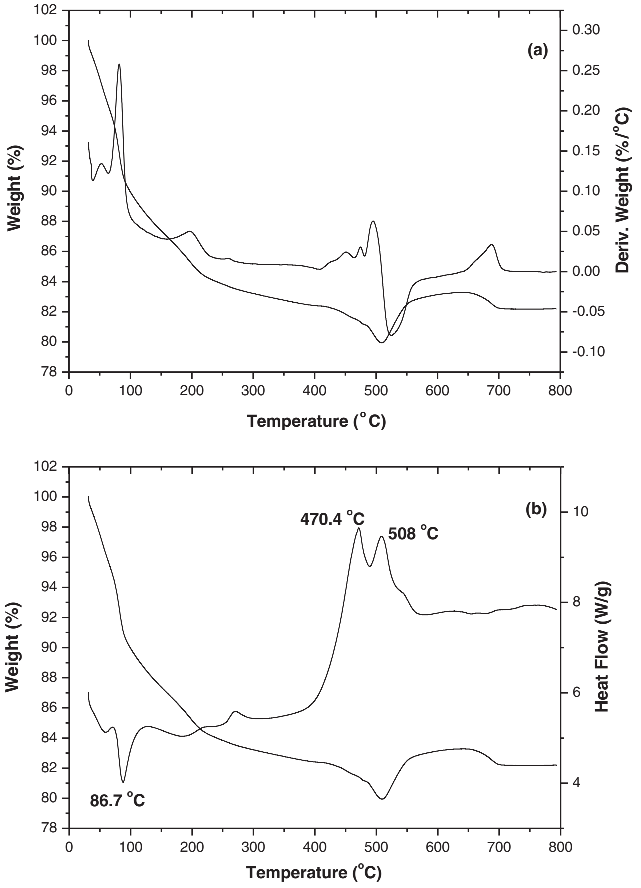

FIGURE 3 TG/DTG analysis of the NiCoP/SiO_2 (Ni: 10 wt.%, Co: 10 wt.%) obtained at 700 °C for 15 min

DTG curves. The weight losses at 494.7 and 528.7 °C in Figure 3a indicate the chemical reaction among NiS, CoS and red P, which is consistent with the exothermic behavior during the reaction among NiS, CoS and red P in Figure 3b. The chemical reactive equation is expressed as follows:

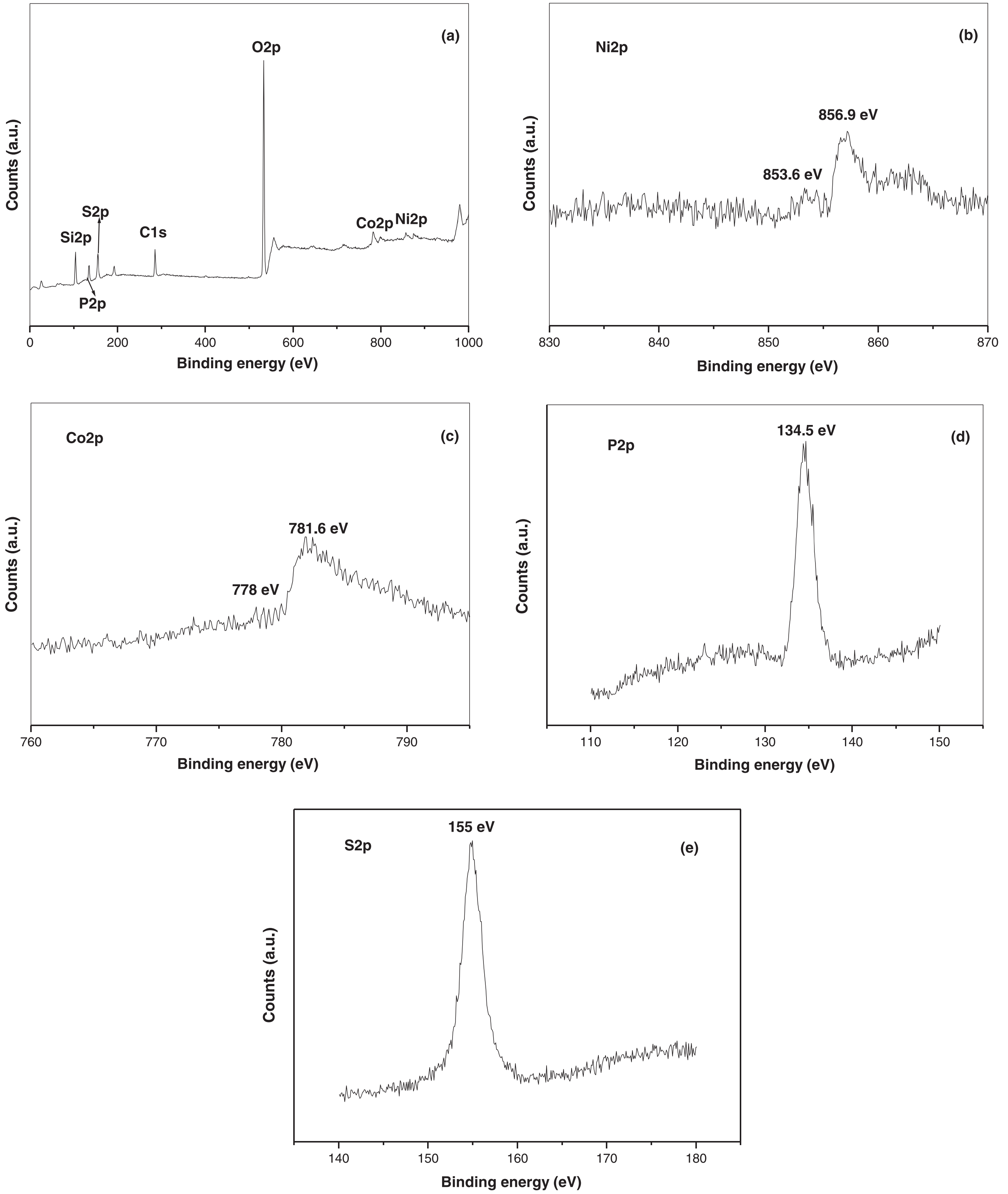

FIGURE 4 XPS spectra of the NiCoP/SiO_2 (Ni: 10 wt.%, Co: 10 wt.%) obtained at 700 °C for 15 min. (a) Survey, (b) Ni2p, (c) Co2p, (d) P2p, (e) S2p

$$P + NiS + CoS = NiCoP + 2S$$

The elemental composition and chemical status of the as-synthesized $NiCoP/SiO_2$ (Ni and Co both 10 wt.%) were further analyzed by X-ray photoelectron spectroscopy (XPS, Figure 4). Figure 4a exhibits the XPS spectrum of $NiCoP/SiO_2$, and the peaks of Si, O, Ni, Co, P, S and C in the sample. The main peaks of Si, O, Ni, Co, and P result from $NiCoP/SiO_2$, and the peak of C results from the additional impurity. The peak of S originates from the S species generated from the M-P-S (NiPS or CoPS) phase, and the sulfur content is 9.55% on the sureface of $NiCoP/SiO_2$. The generated H_2S may react with the product NiCoP to form the M-P-S (NiPS or CoPS) phase in situ at 700 °C. As reported, the M-P-S (NiPS or CoPS) phase is the active material for HDS over metal phosphides.[15,16] Therefore, the formation of S species during the reaction among NiS, CoS and red P may help to enhance the HDS ability of $NiCoP/SiO_2$. The typical high-resolution XPS spectra of Ni2p, Co2p, and P2p are shown in Figure 2b-2d, respectively. The binding energies for Ni (856.9 eV), Co (781.6 eV) and P (134.5 eV) are consistent with the corresponding Ni^{2+}, Co^{2+} and P^{5+} species.[17,18] The surface impurities are generated from air oxidation. The binding energies for 853.6, 778, and 129.5 eV in the sample correspond to Ni2p3/2, Co2p3/2, and P2p3/2 of NiCoP, respectively.[17,18] The XPS peak intensities of Ni2p3/2, Co2p3/2, and P2p3/2 are very lower than those of the oxidized species. During the preparation of the $NiCoP/SiO_2$ catalyst, deioned water was used to wash away the impurities, which might induce severe oxidation on the catalyst's surface. Nevertheless, the $NiCoP/SiO_2$ catalyst was reduced before HDS, which removed the surface oxidation layer, and thus did not affect the HDS capability over $NiCoP/SiO_2$.

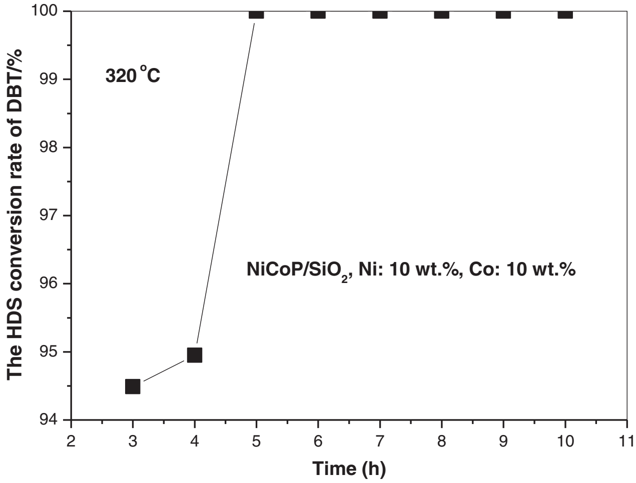

FIGURE 5 The HDS activity for DBT of the $NiCoP/SiO_2$ (Ni: 10 wt.%, Co: 10 wt.%) obtained at 700 °C for 15 min

3.2 | HDS activity of catalysts

The elements of the as-synthesized $NiCoP/SiO_2$ (Ni and Co both 10 wt.%) were analyzed by ICP-AES. The Ni: Co: P molar ratio is 1.3:0.87:1 ($Ni_{1.3}Co_{0.87}P$). The BET specific surface area of $NiCoP/SiO_2$ is 16.4 m^2/g, the pore volume is 0.016 cm^3/g. Figure 5 shows the catalytic data for HDS of DBT over the reduced $NiCoP/SiO_2$ (Ni: 10 wt.%, Co: 10 wt.%) catalyst. The DBT conversion ratio was stable and reached 100% after 5 h. In our previous study,[19] the HDS activity is 73.44% after 9 h using the $NiCoP/SiO_2$ (Ni: 10 wt.%, Co: 10 wt.%) based on metal oxides under the same experimental condition. The result shows that the $NiCoP/SiO_2$ obtained from metal sulfides has higher HDS activity. The presence of S species in the $NiCoP/SiO_2$ from metal sulfides is responsible for the high HDS ability. The major products from DBT conversion determined by GC-MS are biphenyl and benzene. The products contain about 80% biphenyl and the proportion increases with reaction time (Table 1). The composition of products changes significantly when the $NiCoP/SiO_2$ based on metal oxides is used.[19] This result indicates that S species impacts not only the HDS activity, but also the product composition. The S content in the catalyst before and after HDS reaction was 1.16% and 3.45%, respectively. The generated sulfur in the HDS reaction reacted with the catalyst surface lead to increased sulfur content. At the same time, the increased sulfur content means that more active phase of the M-P-S (NiPS or CoPS) may be generated.

4 | CONCLUSIONS

The $NiCoP/SiO_2$ catalyst with higher HDS ability based on metal sulfides was successfully prepared. During the preparation, the generated S species might produce an M-P-S (M: Ni or Co) active phase, which probably enhanced the HDS performance of $NiCoP/SiO_2$.

TABLE 1 GC-MS analysis of the main products of DBT HDS over $NiCoP/SiO_2$ (Ni: 10 wt.%, Co: 10 wt.%)

Retention time (min)	8.731	9.843	10.419	11.185	15.350
HDS products	9-Tetradecen-1-ol	Cyclohexanone	Benzene	Biphenyl	Benzidine

Therefore, this paper provides a new route for synthesis of bimetal phosphides with high HDS ability.

CONFLICT OF INTEREST

Limin Song has received research grants from Tianjin Science and Technology Commission. We have a conflict of interest for applying for a patent.

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REFERENCES

[1] J. S. Thomson, J. B. Green, T. B. Mewilliams, *Energy Fuel* **1997**, *11*, 909.

[2] J. A. C. Fam, S. C. B. Ana, *Catal. Today* **2006**, *118*, 402.

[3] R. L. Leo, M. Boudart, *Science* **1973**, *181*, 547.

[4] Y. Liu, C. Liu, G. Que, *Energy Fuel* **2002**, *16*, 531.

[5] S. Carenco, D. Portehault, C. Boissière, N. Mézailles, C. Sanchez, *Chem. Rev.* **2013**, *113*, 7981.

[6] N. P. Sweeny, C. S. Rohrer, O. W. Brown, *J. Am. Chem. Soc.* **1958**, *80*, 799.

[7] J. A. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López, *J. Catal.* **2009**, *263*, 4.

[8] J. A. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López, *Appl. Catal. Environ.* **2009**, *92*, 100.

[9] W. R. A. M. Robinson, J. N. M. Van Gestel, T. I. Koranyi, *J. Catal.* **1996**, *161*, 539.

[10] Z. W. Yao, H. Hai, Z. C. Lai, X. H. Zhang, F. Peng, C. F. Yan, *Top. Catal.* **2012**, *55*, 1040.

[11] Z. Wu, F. Sun, W. Wu, *J. Catal.* **2004**, *222*, 41.

[12] L. N. Ding, Y. Y. Shu, A. Q. Wang, M. Y. Zheng, L. Li, *J. Appl. Catal. A: General.* **2010**, *385*, 232.

[13] F. X. Sun, W. C. Wu, Z. L. Wu, J. Guo, Z. B. Wei, L. Song, D. Liu, S. Zhang, *J. Catal.* **2004**, *228*, 298.

[14] A. F. Gaudette, A. W. Burns, R. H. John, M. C. Smith, R. H. Bowker, T. Seda, et al., *J. Catal.* **2010**, *272*, 18.

[15] S. T. Oyama, X. Wang, Y. K. Lee, K. Bando, F. G. Requejo, *J. Catal.* **2002**, *210*, 207.

[16] K. A. Layman, M. E. Bussell, *J. Phys. Chem. B* **2004**, *108*, 10930.

[17] I. I. Abu, K. J. Smith, *J. Catal.* **2006**, *241*, 356.

[18] A. W. Burns, K. A. Layman, D. H. Bale, M. E. Bussell, *Appl. Catal. A: General* **2008**, *343*, 68.

[19] S. J. Zhang, L. M. Song, X. Q. Wu, S. Fang, *Vacuum* **2014**, *108*, 45.

How to cite this article: Song L, Liu D, Zhang S. A novel route for synthesis of NiCoP/SiO_2 hydrodesulfurization catalysts with active S species. *Appl Organometal Chem*. 2018;e4306. https://doi.org/10.1002/aoc.4306