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PAPER

The synthesis and evaluation of highly active Ni_2P–MoS_2 catalysts using the decomposition of hypophosphites

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This paper presents the synthesis and evaluation of highly active Ni_2P–MoS_2 catalysts using the decomposition of hypophosphites. A family of catalysts have been prepared, whose activities were tested using the hydrodesulfurization of 4,6-dimethyldibenzothiophene. Furthermore, the synergy between Ni_2P/Al_2O_3 and MoS_2/Al_2O_3 beds was explained by the remote control model through a migration of hydrogen spillover.

1. Introduction

As a consequence of economic development, cars have become essential to people's lives in most countries. Naturally, the automobile exhaust has become a serious source of pollution in recent decades. For example, the combustion products of sulphur and nitrogen compounds in gasoline and diesel fuel will cause enormous damage to our environment. Energy saving and emission reduction will remain hot issues over the next few decades or even hundreds of years. Hence, most countries have enacted stringent environmental regulations to limit sulphur and nitrogen levels in gasoline and diesel fuel.[1] Effective deep hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) techniques have never been as urgent as they are now. However, the improvement of traditional sulfide catalysts has had difficulty in achieving the required level for effective desulfurization and denitrogenation. As a new class of catalytic materials, metal phosphides have attracted considerable attention because of their excellent activity for HDS and HDN.[2] It is essential to do further in-depth studies of metal phosphide catalysts.

It is well known that there are many ways to synthesize metal phosphides. These include temperature-programmed reduction of metal phosphates[2] or metal phosphites,[3,4] solvothermal reactions,[5] decomposition of single-source precursors,[6] high-temperature annealing of preformed nanoparticle precursors,[7] the reduction of metal oxide nanoparticles by PH_3/H_2,[8] the reaction of trioctylphosphine (TOP) with metal salts,[9] the conversion of preformed metal nanoparticles into metal phosphides by solution-mediated reaction with TOP,[10] the decomposition of nickel thiophosphate ($NiPS_3$),[11,12] the reduction of oxide precursors in a hydrogen plasma,[13] the decomposition of metal hypophosphites,[14–16] and the synthesis of Ni_2P/SiO_2 by palladium addition.[17]

In this paper, we conducted a further detailed investigation of our previously proposed methods.[15] A family of catalysts have been prepared, whose activities were tested using the hydrodesulfurization of 4,6-DM-DBT. Furthermore, the synergy between Ni_2P/Al_2O_3 and MoS_2/Al_2O_3 beds was explained by the remote control model. For comparison, commercial NiWMoS catalyst was also tested under the same HDS conditions.

2. Experimental methods

Alumina (Tianjin Research Institute of Chemical Industry) was calcined at 600 °C for 3 h and had a specific surface area of 212 m^2 g^{-1}, a pore volume of 0.39 cm^3 g^{-1}, and a Barrett–Joyner–Halenda (BJH) average pore size of 4.8 nm. Siliceous MCM-41 (Tianjin Chemist Scientific Ltd) had a specific surface area of 956 m^2 g^{-1}, a pore volume of 1.1 cm^3 g^{-1}, and a Barrett–Joyner–Halenda (BJH) average pore size of 3.32 nm. 4,6-Dimethyl-dibenzothiophene (4,6-DM-DBT) was analytical pure grade and purchased from Alfa Aesar. Commercial NiWMoS catalyst and the corresponding Al_2O_3 carrier were purchased from Shandong Qilu Petrochemical Engineering Co. Ltd. Because of technical secrets, their detailed compositions were not provided by the company. Other reagents were analytical pure grade and purchased from Tianjin Guangfu Fine Chemical Research Institute, China.

2.1. Synthesis of supported catalysts

Supported metal phosphides on MCM-41 containing 10 wt% of metal and denoted Ni_2P/MCM, MoP/MCM, WP/MCM and Cu_3P/MCM were obtained as follows. Metal chloride (or other nonoxidizing metal salts) and sodium hypophosphite were dissolved in deionized water. Then, a certain amount of support was added to the solution, and the mixture was slowly stirred for 2 h. Subsequently, the slurry was evaporated slowly to dehydrate to get the precursor, which was dried at 80 °C for 8 h. Initially, the air in the reactor was removed by flowing Ar (or N_2), after which the precursor was treated at the required temperature for 0.5 h in a static Ar atmosphere.

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The product was cooled to ambient temperature under Ar and was washed several times with deionized water to remove ionic impurities, after which the wet material was dried at 120 °C for 3 h.

Supported MoS_2 catalysts containing 5 wt% of Mo denoted MoS_2/Al and MoS_2/MCM, when supported on Al_2O_3 and MCM-41, respectively, were obtained as follows. Ammonium molybdate ((NH_4)$_6Mo_7O_{24}\cdot 4H_2O$) and 28 times (mole ratio) thioacetamide (CH_3CSNH_2) were dissolved in deionized water with stirring. The resultant solution reacted in a 90 °C water bath for 30 min to obtain a MoS_4^{2-} solution. Then, a certain amount of support was added to the solution, and the mixture was slowly stirred for 2 h. Subsequently, the solution was evaporated slowly to dehydrate the product, which was then dried at 80 °C to obtain the precursor. Finally, the precursor was treated at 250 °C for 1 h and 380 °C for 1 h in an Ar atmosphere.

Supported Ni–MoS_2 catalysts containing 2 wt% of Ni and 5 wt% of Mo denoted Ni–MoS_2/Al and Ni–MoS_2/MCM, when supported on Al_2O_3 and MCM-41, respectively, were obtained as follows. A certain amount of nickel nitrate was first dissolved in deionized water with magnetic stirring to form a clear solution. Subsequently, supported MoS_2 was added to the solution and stirred for 1 h. Then, the slurry was evaporated at 120 °C to obtain the precursor. Subsequently, the precursor was heated at 300 °C for 1 h in a static Ar atmosphere. Finally, the product was cooled to ambient temperature under flowing Ar, and was passivated for 3 h under flowing 1% O_2/N_2.

Supported Ni_2P–MoS_2 catalysts containing 2 wt% of Ni_2P and 5 wt% of Mo denoted Ni_2P–MoS_2/Al and Ni_2P–MoS_2/MCM, when supported on Al_2O_3 and MCM-41, respectively, were obtained as follows. NaH_2PO_2 and $NiCl_2$ in a mole ratio of 1.5 were dissolved in deionized water with magnetic stirring to form a clear solution. Subsequently, supported MoS_2 was added to the solution and stirred for 1 h. Then, the slurry was evaporated slowly to dehydrate the product, which was dried at 80 °C to obtain the precursor. Subsequently, the precursor was heated at 300 °C for 0.5 h in a static Ar atmosphere. Finally, the product was cooled to ambient temperature under flowing Ar, washed three times with deionized water, and dried at 120 °C for 3 h.

2.2. Characterization and catalytic activity test

Powder X-ray diffraction was performed on a Rigaku D/Max-2500 diffractometer, with Cu Kα radiation at 40 kV and 100 mA. The compositions of the sample were measured by inductively coupled plasma–atomic emission spectroscopy (ICP–AES). Transmission electron microscopy (TEM) images were acquired using a Philips Tecnai G^2 F-20 field emission gun transmission electron microscope. Nitrogen adsorption–desorption isotherms of samples at 77 K were measured with a BEL-MINI adsorption analyzer. The HDS catalytic activities were evaluated using 3000 ppm 4,6-DM-DBT in decalin. The catalyst was pelleted, crushed, and sieved with a 20–40 mesh. 1.00 g of the catalyst was diluted with SiO_2 to a volume of 5.0 mL in the reactor. The HDS reaction was carried out at 3 MPa in a continuous-flow fixed-bed microreactor. Liquid products were collected every hour after a stabilization period of 6 h.

Both feed and products were analyzed with a FULI 9790 gas chromatograph equipped with a flame ionization detector and an OV-101 column.

3. Results and discussion

3.1. Synthesis of supported catalysts

In previous studies, Ni_2P can be synthesized easily from the thermal decomposition of hypophosphites at 250 °C in 10 min,[15] and the synthesis is not affected by the heating rates. As shown in Fig. 1, bulk Ni_2P could be synthesized from the mixed-salt precursor, with NaH_2PO_2 and $NiCl_2$ at (P/Ni) molar ratios between 1.5 and 1.75. In this paper, the synthesis conditions of the bulk and supported nickel phosphide are identical. The diffraction peaks of Ni_5P_4 were detected at a molar ratio of 2.0. Fig. 2 shows the catalytic activity of Ni_2P/MCM catalysts prepared with different (P/Ni) molar ratios. Corresponding well with the results of Fig. 1, the catalyst prepared with a molar ratio of P/Ni = 1.5 has the highest conversion of 4,6-DM-DBT. The conversion of 4,6-DM-DBT decreased with the increase in the P/Ni molar ratio, which might be caused by the generation of Ni_5P_4. The results also indicate
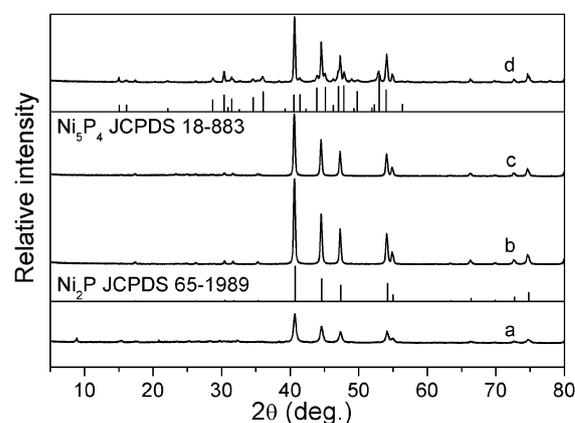

Fig. 1 The XRD patterns of bulk nickel phosphide prepared from the precursors, which consist of NaH_2PO_2 and $NiCl_2$ with different (P/Ni) molar ratios: (a) 1.33, (b) 1.50, (c) 1.75, (d) 2.0.
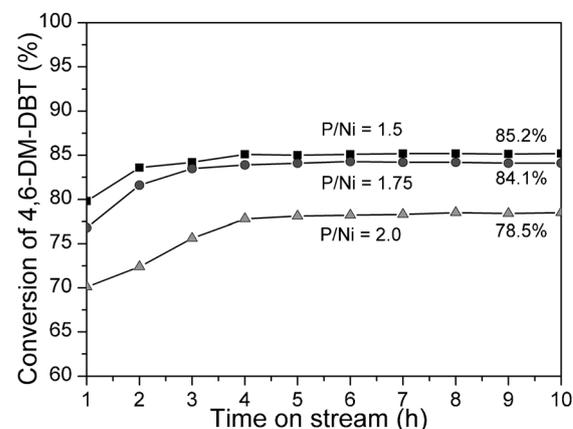

Fig. 2 The catalytic activity of Ni_2P/MCM catalysts prepared with different (P/Ni) molar ratios (testing conditions: 3 MPa, 350 °C, WHSV = 6 h^{-1}, H_2/oil = 720).
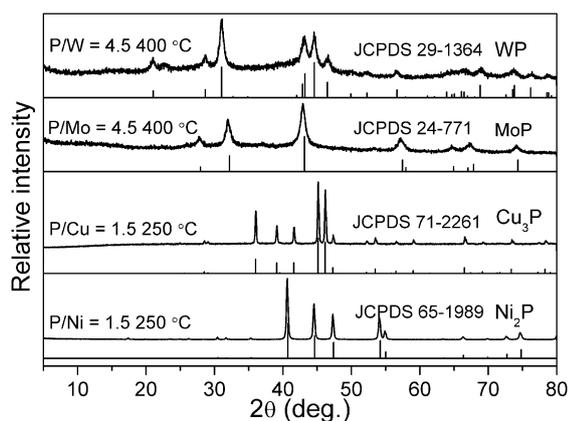
Fig. 3 The XRD patterns of bulk metal phosphides from the thermal decomposition of hypophosphites.

that the optimal synthesis conditions of supported nickel phosphides were similar to those of bulk nickel phosphides. In the synthesis of supported metal phosphides, excess phosphorus was not needed compared to bulk metal phosphides. This may be due to the fact that the mixture is a relatively uniform mixture of metal ions and hypophosphite in the ionic state, and the precursor was heated at 300 °C for 1 h in a static Ar atmosphere. Therefore, phosphorus can be fully utilized during the reaction.

A family of bulk catalyst have been prepared from the thermal decomposition of hypophosphites, the optimal mole ratios and calcination temperatures are given in Fig. 3. The typical diffraction peaks of different metal phosphides are clearly shown, which are close to the corresponding values reported in the Joint Committee on Powder Diffraction Standards (JCPDS). The XRD result indicates that bulk Ni_2P, Cu_3P, MoP, and WP could be synthesized from the thermal decomposition of hypophosphites. In previous studies, a series of Ni_2P/MCM-41 catalysts with different loadings have been successfully prepared by treating MCM-41-supported mixed salt precursors.[15] The XRD diffraction peaks of Ni_2P were not detected at the loadings of 10 wt% and 15 wt%, which might be because the Ni_2P nanoparticles were so tiny and lower than the detection limit.

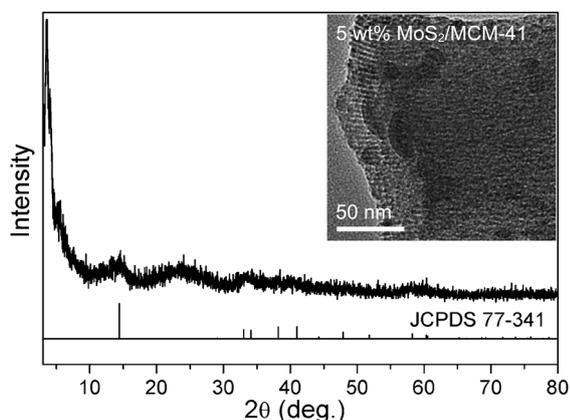The supported MoS_2 could be easily synthesized from the decomposition of $(NH_4)_2MoS_4$/MCM-41. Fig. 4 shows the

XRD pattern and TEM image of MoS_2/MCM. Only very weak diffraction peaks of MoS_2 were detected in the XRD pattern, which might be caused by low loading (5 wt%) and/or high dispersion on MCM-41. The TEM image of MoS_2/MCM shows that the particle size of MoS_2 was not longer than 5 nm. Similarly, the diffraction peaks of Ni_2P were not detected from Ni_2P–MoS_2/MCM. The XRD patterns of all supported metal phosphide catalysts are not given in this paper. The loading of metal phosphide in supported catalysts was 10 wt%, which is highly dispersive and lower than the XRD detection limit.

3.2. HDS activity

The catalytic activities of different catalysts were tested by the removal of sulphur from 4,6-DM-DBT in the HDS reaction. Fig. 5 shows the catalytic activity of Ni_2P/MCM-41 catalysts with different loadings (testing conditions: 3 MPa, 350 °C, WHSV = 6 h^{-1}, H$_2$/oil = 720). The results indicate that the catalytic activities of Ni_2P/MCM-41 catalysts increased with the increasing Ni_2P loading. The conversion of 4,6-DM-DBT is 85.2, 94.8, 99.1, and 100% for 10, 15, 20, 32 wt% Ni_2P/MCM-41 catalysts, respectively. As shown in Fig. 6, Oyama *et al.* have reported the products of 4,6-DM-DBT desulfurization for phosphide catalysts.[18] The selectivity of the reaction was calculated using the products, which mainly included 3,3′-dimethylbiphenyl (DMBP), 3-methylcyclohexyltoluene (MCHT), and 3,3′-dimethylbicyclohexane (DMBCH). As shown in Table 1, all of the catalysts were tested under the same conditions (3000 ppm 4,6-DM-DBT in decalin, 3 MPa, WHSV = 6 h^{-1}, H$_2$/oil = 720). Conversions for different metal phosphide catalysts indicate that Ni_2P/MCM had the best catalytic activities. The activities of all metal phosphide catalysts increased with the increasing reaction temperature. The activities of the metal phosphide catalysts followed the order Ni_2P/MCM > MoP/MCM > WP/MCM > Cu_3P/MCM. The results indicated that all of the metal phosphide catalysts favor desulfurization by the HYD route at 350 °C. Besides, MoS_2, Ni–MoS_2, and Ni_2P–MoS_2 catalysts supported on a commercial support, Al_2O_3, and on a mesoporous material, MCM-41, were also prepared and the corresponding catalyst composition and
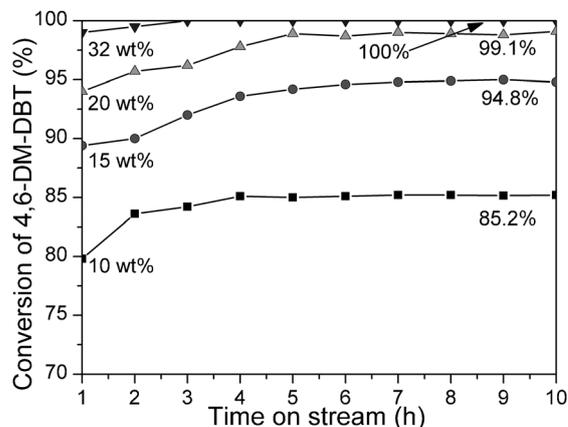

Fig. 4 The XRD patterns and TEM image of MoS_2/MCM.

Fig. 5 The catalytic activity of Ni_2P/MCM-41 catalysts with different loadings (testing conditions: 3 MPa, 350 °C, WHSV = 6 h^{-1}, H$_2$/oil = 720).

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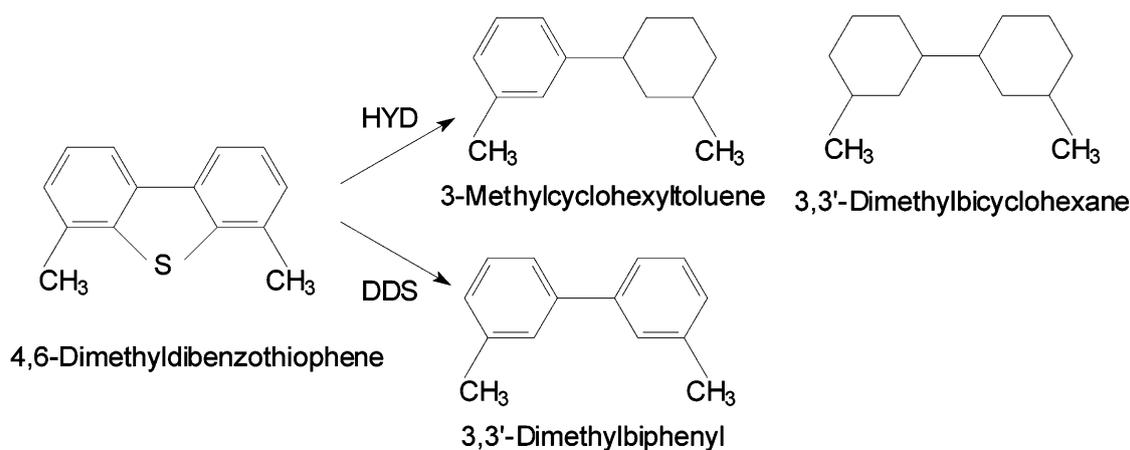This journal is © The Royal Society of Chemistry 2012

Fig. 6 The products of 4,6-dimethyldibenzothiophene desulfurization.

Table 1 HDS catalytic activity of different catalysts (testing conditions: 3 MPa, WHSV = 6 h^{-1}, H$_2$/oil = 720)

Catalysts	Conversion (%)			Selectivity at 350 °C (%)		
	310 °C	330 °C	350 °C	DMBP	MCHT	DMBCH
Ni$_2$P/MCM	72.3	78.4	85.2	36.9	54.6	8.5
MoP/MCM	54.6	56.3	58.6	28.9	57.0	14.1
WP/MCM	42.8	46.1	49.4	32.3	58.5	9.2
Cu$_3$P/MCM	25.5	32.0	36.2	20.5	66	13.5
MoS$_2$/MCM	63.3	63.7	64.0	23.7	64.0	12.3
Ni–MoS$_2$/MCM	81.2	82.6	85.2	27.5	63.3	9.2
Ni$_2$P–MoS$_2$/MCM	86.6	88.3	93.8	12.8	81.5	5.7
MoS$_2$/Al	75.3	76.2	76.8	13.5	79.1	7.4
Ni–MoS$_2$/Al	90.4	91.3	92.8	7.1	87.3	5.6
Ni$_2$P–MoS$_2$/Al	97.8	100	100	5.3	92.1	2.6
Ni$_2$P/Al//MoS$_2$/Al	97.3	99.5	100	5.8	91.5	2.7
MoS$_2$/Al//Ni$_2$P/Al	76.1	76.9	77.9	13.4	79.1	7.5
NiWMoS	67.6	85.4	95.7	5.9	76.9	17.2

nomenclature included in Table 1. Interestingly, both MCM-41 and commercial Al$_2$O$_3$ supported Ni$_2$P–MoS$_2$ catalysts show higher activity than individual MoS$_2$, and Ni–MoS$_2$ catalysts. The Ni$_2$P–MoS$_2$/Al showed the highest activities, which is even higher than the commercial NiWMoS catalyst. The results also show that catalysts supported on commercial Al$_2$O$_3$ have higher activity than that supported on MCM-41. Table 2 shows the textural properties of Ni$_2$P–MoS$_2$/Al and Ni$_2$P–MoS$_2$/MCM, and the Ni$_2$P–MoS$_2$/Al catalyst has a lower BET surface area and a larger BJH pore size. The results indicate that the larger pore size is more conducive to the HDS reaction, which might

Table 2 Properties of different catalysts

Catalysts	BET surface area/m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Average pore size/nm
MCM-41	956	1.1	3.3
Ni$_2$P–MoS$_2$/MCM (fresh)	752	0.9	3.3
Ni$_2$P–MoS$_2$/MCM (after 72 h)	748	0.9	3.3
Al$_2$O$_3$	226	0.39	4.8
Ni$_2$P–MoS$_2$/Al (fresh)	202	0.31	4.8
Ni$_2$P–MoS$_2$/Al (after 72 h)	201	0.31	4.8

facilitate the diffusion of the reactant molecules in the pore of the support. Moreover, many published papers have reported that acidic supports can increase the conversion of dibenzothiophene (DBT) and of 4,6-DM-DBT.[19] The possible explanation for this improvement is the creation of a second hydrogenation pathway by spillover of hydrogen atoms from the metal particles to the aromatic sulphur-containing molecules that are adsorbed on acidic sites in the vicinity of the metal particles.[20–22] As we all know, Al$_2$O$_3$ has weak acid sites, which is beneficial to the HDS reaction.

The interesting results also indicate that commercial Al$_2$O$_3$ for the HDS reaction was suitable for the preparation of metal phosphide catalysts in this method. To further explain the high activity of Ni$_2$P–MoS$_2$/Al, the "separated bed" experiments were used to show the synergy between Ni$_2$P/Al and MoS$_2$/Al. Similar to the published report,[23] the "separated bed" tests were carried out as follows: (a) in a HDS fixed-bed microreactor, a three-layer system was prepared, 1 g 2 wt% Ni$_2$P/Al$_2$O$_3$ was filled in the up bed and 1 g 5 wt% MoS$_2$/Al$_2$O$_3$ was filled in the down bed. Both beds were separated by a 0.5 cm quartz fibres layer. This separated bed was denoted Ni$_2$P/Al//MoS$_2$/Al. (b) In this test, the samples were of the same amount but located in the opposite position compared to the test (a), which was denoted MoS$_2$/Al//Ni$_2$P/Al. The separated bed test results are given in Table 1, HDS conversion obtained with the Ni$_2$P/Al//MoS$_2$/Al bed is much higher than that obtained with MoS$_2$/Al, and MoS$_2$/Al//Ni$_2$P/Al. The results unequivocally demonstrate that the synergism is mainly a consequence of a remote control phenomenon through a migration of hydrogen spillover. The catalytic activity of Ni$_2$P–MoS$_2$/Al is higher than that of Ni–MoS$_2$/Al, which indicated that Ni$_2$P has a higher hydrogen dissociation activity than Ni. Limited by the laboratory conditions, the stabilities for Ni$_2$P–MoS$_2$/Al and Ni$_2$P–MoS$_2$/MCM catalysts were only tested at 330 °C for 72 h, which shows both catalysts have good stabilities. Table 2 shows the properties of different catalysts. Both MCM-41 and Al$_2$O$_3$ supported Ni$_2$P–MoS$_2$ catalysts almost have little change after being used for 72 h, which indicates that these catalysts may have excellent stability.

4. Conclusions

This paper presents the synthesis and evaluation of highly active Ni$_2$P–MoS$_2$ catalysts using the decomposition of hypophosphites.

A family of catalysts have been prepared, whose activities were tested using the hydrodesulfurization of 4,6-dimethyldibenzothiophene. The activities of the metal phosphide catalysts followed the order $Ni_2P/MCM > MoP/MCM > WP/MCM > Cu_3P/MCM$. The 4,6-DM-DBT conversion results indicate that all of the metal phosphide catalysts favor desulfurization by the HYD route at 350 °C. Furthermore, $Ni_2P–MoS_2/Al_2O_3$ presented the highest activities, which is even higher than the commercial NiWMoS catalyst. The synergy between Ni_2P/Al_2O_3 and MoS_2/Al_2O_3 beds was explained by the remote control model through a migration of hydrogen spillover. These studies provide a possibility of large-scale applications of metal phosphide composite catalysts in the HDS reaction.

Acknowledgements

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