Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Catalysis 229 (2005) 314–321

JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Hydrodesulfurization of dibenzothiophene over siliceous MCM-41-supported nickel phosphide catalysts

Anjie Wang [a,b,*], Lifeng Ruan [a], Yang Teng [a], Xiang Li [a,b], Mohong Lu [a], Jing Ren [a], Yao Wang [a,b], Yongkang Hu [a,b]

[a] *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, P.R. China*
[b] *Liaoning Key Laboratory of Petrochemical Technology and Equipments, Dalian University of Technology, Dalian 116012, P.R. China*

Received 27 July 2004; revised 19 September 2004; accepted 22 September 2004

Abstract

Siliceous MCM-41-supported nickel phosphides from a precursor with a Ni/P atomic ratio of 3, 2, 1.25, 1, 0.5, or 1/3 were prepared by in situ reduction. A high heating rate and a multistep program were used to prepare the supported nickel phosphides. The in situ reduction method proved superior to the traditional reduction–passivation–rereduction method. The timely removal of local moisture from the surface during reduction is crucial to obtaining a high hydrodesulfurization (HDS) performance of the phosphide catalysts. The precursors were characterized by TPR to investigate the reactions involved in phosphide preparation, and the structures of the resulting nickel phosphides were characterized by means of ^{31}P NMR and XRD. Nickel phosphide formation may start with the reduction of NiO to Ni, and the Ni metal may assist phosphide formation in the reduction of nickel-rich precursors. Nickel-rich phosphides exhibited much higher HDS activity than phosphorus-rich phosphides prepared by the in situ reduction method. Reduction of the precursor with $Ni/P = 2$ yielded $Ni_{12}P_5$/MCM-41, whereas reduction of the precursor with $Ni/P = 1.25$ produced Ni_2P/MCM-41. As in the traditional reduction–passivation–rereduction method, a small excess of phosphorus in the precursors is also needed to obtain the desired nickel-rich phosphides by the in situ reduction method. Ni_2P/MCM-41 was the most active catalyst in the HDS of dibenzothiophene among all of the supported nickel phosphides prepared by the in situ reduction method.

Keywords: Hydrodesulfurization; Nickel phosphide; In situ reduction; MCM-41; Dibenzothiophene

1. Introduction

Traditional hydrodesulfurization (HDS) catalysts are alumina-supported Mo or W sulfides promoted by Ni or Co. The need to produce clean engine fuels, combined with the prospect of processing poor-quality petroleum feedstocks, has stimulated the development of high-performance HDS catalysts. One of the approaches to improving HDS catalysts is to find new active phases by including other cations (e.g., Ru, Pt, Pd) and anions (e.g., carbides, nitrides) [1]. Transition metal phosphides have recently been reported to be promising as a new class of high-performance hydroprocessing catalysts. Among the phosphides studied, MoP and WP were reported to be more active than the corresponding group VI metal sulfides [2–4]. Ni_2P was found to be the most active phase in the iron group compounds, although Fe_2P, CoP, and Co_2P also showed substantial HDS activities [5–9]. Moreover, Ni_2P showed higher HDS and HDN activities than MoP or WP [10].

Whereas alumina is a very good carrier for supported sulfides, it is an inferior carrier for metal phosphides because it reacts with phosphate to form aluminum phosphates on the surface [11–13]. Silica was reported to be a superior support because of its weak interaction with phosphates [8]. We have successfully prepared high-activity HDS catalysts by supporting Mo- or W-based sulfides on siliceous MCM-41

---

[*] Corresponding author. Fax: +86-411-88993991.
E-mail address: anjwang@chem.dlut.edu.cn (A. Wang).

0021-9517/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2004.09.022

[14–16]. The surface properties of siliceous MCM-41 are supposed to be similar to those of silica, but MCM-41 has a much higher surface area, which guarantees a high dispersion of the active phases. Therefore, siliceous MCM-41 was used to support nickel phosphides in this study.

2. Experimental

2.1. Catalyst preparation

Siliceous MCM-41 was synthesized with the use of sodium silicate hydrate as the SiO_2 source and cetyltrimethylammonium bromide as the template, following a procedure reported elsewhere [17]. The synthesized siliceous MCM-41 has a specific surface area of 1046 $m^2\ g^{-1}$, a pore volume of 0.95 $cm^3\ g^{-1}$, and a BJH average pore size of 3.8 nm. MCM-41-supported nickel phosphides were prepared according to a procedure adapted from the literature [5,12,18]. The procedure mainly includes two steps: (1) the oxidic precursor was obtained by co-impregnation with an aqueous solution of diammonium hydrogen phosphate $[(NH_4)_2HPO_4]$ and nickel nitrate, followed by drying and calcination; (2) the precursor was converted to nickel phosphide in flowing H_2 by temperature-programmed reduction. The sum of the loadings of NiO and P_2O_5 was chosen to be 20 wt% for all of the supported precursors, except when we investigated the effect of loading. The Ni/P atomic ratios of the precursors were 3, 2, 1.25, 1, 1/2, and 1/3. They are denoted as Ni–P(x), where x represents the Ni/P atomic ratio in the precursor. All of the precursors were prepared with the same procedure, except that the masses of $Ni(NO_3)_2$ and $(NH_4)_2HPO_4$ varied with Ni/P ratio. As an example, the preparation of Ni_2P/MCM-41 is illustrated as follows. One gram of $(NH_4)_2HPO_4$ was dissolved in 20 ml of deionized water to form a transparent colorless solution, and then 4.4 g $Ni(NO_3)_2 \cdot 6H_2O$ was added. The clear solution immediately became cloudy, but, when the pH of the mixture was adjusted to 2–3 with 0.5 M HNO_3, it became clear again. Three grams of siliceous MCM-41 was evacuated for 0.5 h and then wet-impregnated with the prepared solution for 0.5 h at room temperature. Then the water was evaporated and the solid product was dried at 120 °C overnight, followed by calcination in air at 540 °C for 3 h.

In contrast to the reduction method reported in the literature, a new reduction method was used in our study. Prior to the HDS reaction, the oxidic precursor was reduced in situ in flowing H_2 in the HDS reactor by a temperature-programmed procedure.

2.2. In situ reduction and HDS catalysis measurements

The conversion of the precursor to the metal phosphide and the HDS reaction were carried out in the same continuous-flow tubular microreactor. The oxidic precursor was pelleted, crushed, and sieved to 20–35 mesh. The precursor (0.2 g) was charged in each run. The nickel phosphides were prepared in situ by temperature-programmed reduction in the reactor prior to HDS reaction. A high heating rate (2.5–5 °C min^{-1}) was used, and the flow rate of H_2 was varied from 100 to 250 $cm^3\ min^{-1}$. In general, a high H_2 flow rate and a high heating rate were used at low temperature to remove local moisture from the surface of the precursor. After the precursor had been converted to nickel phosphide by reduction, the reactor was cooled to the HDS reaction temperature.

The HDS activities of the prepared catalysts were evaluated with the use of 0.8 wt% dibenzothiophene (DBT) in decalin as model feed. DBT was synthesized from biphenyl and sulfur according to a previously published method [19], and decalin was of A.R. grade. The testing conditions for the HDS reaction were 280–340 °C, 5 MPa, WHSV = 24 h^{-1}, and a H_2 flow rate of 130 ml min^{-1} at atmospheric pressure. Sampling of liquid products was started 6 h after the reaction conditions had been achieved. For each run, three to five liquids were collected at an interval of 20 min. Both feed and products were analyzed with an Agilent-6890^+ gas chromatograph equipped with an FID detector and an HP-5 column. Since no sulfur-containing components were detected among the HDS products, the DBT conversion was used as a measure of HDS activity.

2.3. Catalyst characterization

The temperature-programmed reduction (TPR) profiles of MCM-41-supported catalyst precursors were measured on a Chembet-3000 analyzer. Before the measurement, the sample was pretreated in He at 200 °C for 2 h. A gas mixture of 5 vol% H_2 in Ar was used as the reacting agent. The TPR profiles of the catalysts were measured from 100 to 950 °C at 10 °C min^{-1}.

^{31}P NMR spectra and XRD patterns of the supported nickel phosphides were measured to determine the crystal phase on the surface. The supported nickel phosphides were prepared according to the same reduction conditions as used during the in situ reduction, followed by passivation with 0.5% O_2 in Ar. ^{31}P NMR spectra were obtained with a Varian INOVA 400 M NMR spectrometer equipped with a magic-angle-spinning probe. Phosphoric acid (85%) was used as an external reference. Spectra were acquired with the use of a single 1.8-µs pulse causing a flip angle of about $\pi/4$ and a recycle time of 1 s. The measurements were performed at room temperature with 1800 scans. The XRD patterns of the supported catalysts were measured on a Rigaku D/Max 2400 diffractometer with nickel-filtered Cu-K_α radiation at 40 kV and 100 mA.

Nitrogen adsorption was measured with a Quantachrome AUTOSORB-1 adsorption analyzer, which reports adsorption isotherm, BET specific surface area, and pore volume automatically. The samples were outgassed for 4 h at 300 °C before the adsorption.

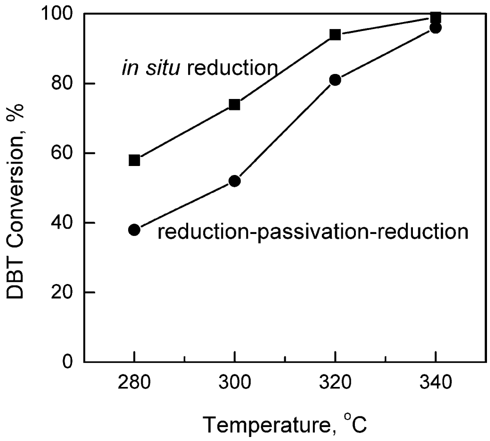

Fig. 1. Comparison of in situ reduction method with traditional reduction–passivation–reduction method in preparing MCM-41-supported nickel phosphide HDS catalysts.

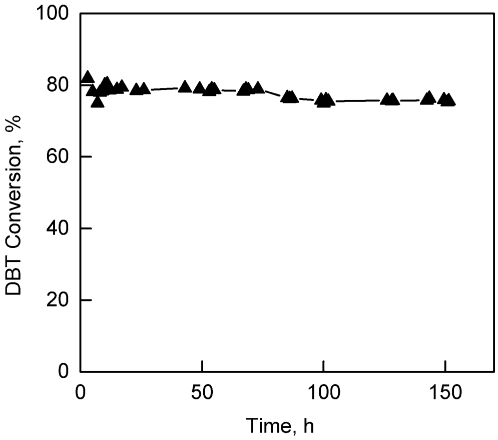

Fig. 2. Activity variation of the supported nickel phosphides prepared from Ni–P(2)/MCM-41 with reaction time in HDS of DBT at 300 °C and 5.0 MPa.

3. Results and discussion

3.1. In situ reduction

Traditionally, the reduction of the oxidic precursor to nickel phosphide and the HDS reaction have been carried out in two separate reactors. To prevent the obtained phosphides from rigorous oxidation when exposed to air, the prepared phosphides were passivated with low-concentration O_2 before they were transferred to the HDS reactor [10]. However, although the passivation slows down the oxidation reaction, the crystal structure of the phosphide might be partly damaged by the oxidation. Therefore, we have studied the in situ reduction process, that is, reduction and HDS reaction taking place sequentially in the same reactor.

Fig. 1 shows a comparison of the HDS activities of the supported Ni–P(2) catalysts prepared by the traditional reduction–passivation–rereduction method and by the in situ reduction method. The reduction conditions were the same in the two methods (H_2 flow rate: 150 ml min^{-1}; heating rate: 2.5 °C min^{-1}; final reduction temperature: 500 °C; reduction time at 500 °C: 3 h). In the reduction–passivation–rereduction, the prepared nickel phosphide was passivated with 0.5% O_2 in Ar at a flow rate of 160 ml min^{-1} for 3 h before it was exposed to air. Before the HDS reaction, the prepared catalysts were rereduced at 500 °C for 2 h in the reactor.

It is shown that the in situ reduction method gave much better results than the traditional reduction method. A possible reason for this is that the crystal structure is well protected because it has not been exposed to air or O_2. Several researchers [5,6,18,20–22] have reported that Ni or Mo phosphides prepared by the traditional reduction method exhibited an increase in HDS activity in the first few hours of time on stream. This increase was not observed in the supported nickel phosphides prepared from Ni–P(2) by in situ reduction (Fig. 2). Therefore, we propose that a small part of the prepared nickel phosphides may be oxidized during passivation, leading to a slight structural loss. When the passivated phosphides catalyze HDS reactions in flowing H_2, their phosphide structures may be reformed, resulting in an improvement in HDS activity.

It is well known that it is essential to use a very high gas space velocity and a low heating rate during the temperature-programmed reaction to synthesize high-performance transition-metal nitrides, carbides, or phosphides. Because the conversion of metal nitride, carbide, and phosphide to their oxides is thermodynamically favorable, rigorous oxidation or sometimes even burning will occur when a metal nitride, carbide, or phosphide is exposed to air or water. Assuming that the key factor in the phosphide preparation is the timely removal of local water vapor (which is a product of the reduction) from the catalyst surface, two reduction programs (Table 1) were designed to

Table 1
Temperature programs used in in situ reduction[a]

Program A	Program B
(1) Heating from room temperature to 400 °C at 5 °C min^{-1}	(1) Heating from room temperature to 120 °C at 5 °C min^{-1}
(2) Retaining for 1 h at 400 °C	(2) Retaining for 1 h at 120 °C (H_2 flow rate was 250 cm^3 min^{-1})
(3) Heating from 400 °C to final reduction temperature at 2.5 °C min^{-1}	(3) Heating from 120 to 400 °C at 5 °C min^{-1}
(4) Retaining for 3 h at final reduction temperature	(4) Retaining for 1 h at 400 °C
	(5) Heating from 400 °C to final reduction temperature at 2.5 °C min^{-1}
	(6) Retaining for 3 h at final reduction temperature

[a] H_2 flow rate was kept at 150 cm^3 min^{-1}, except for the second step in program B.

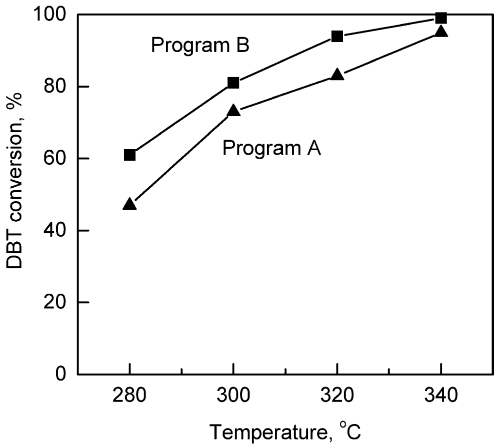

Fig. 3. Comparison of HDS activities prepared from Ni–P(2)/MCM-41 by different reduction temperature programs.

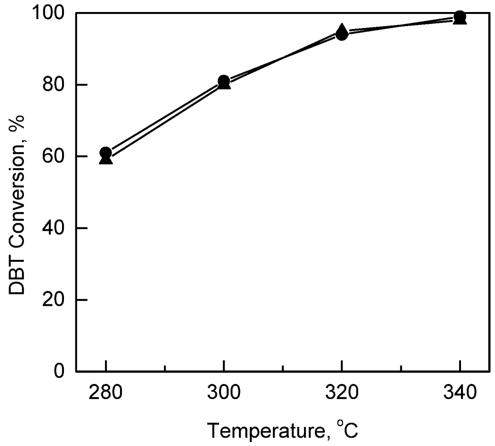

Fig. 4. Effect of flowing gas type at 120 °C on the HDS performance of the prepared nickel phosphides: (▲) H_2 and (●) N_2.

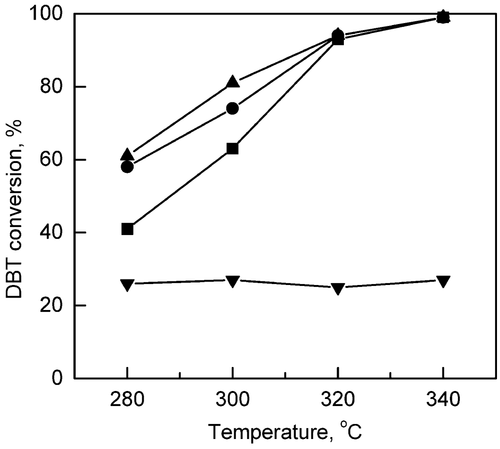

Fig. 5. Dependence of HDS activity on the final temperature during the in situ reduction by program B: (▼) 400, (▲) 500, (●) 600, and (■) 700 °C.

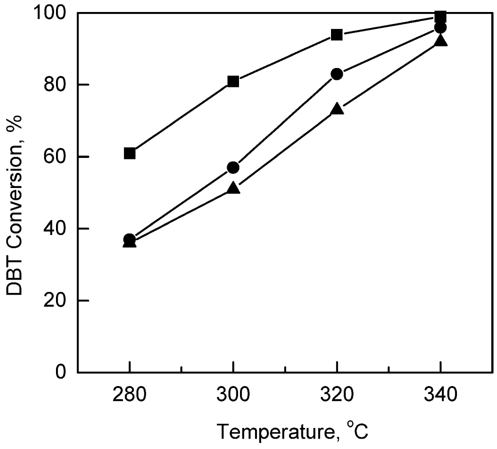

Fig. 6. Effect of gas flow rate at final temperature during in situ reduction by program B on the performance of the prepared nickel phosphides in HDS of DBT: (▲) 65, (●) 150, and (■) 250 $cm^3\ min^{-1}$.

investigate the effects of preparation conditions. In contrast to program A, the temperature was kept constant at 120 °C for 1 h and a higher H_2 flow rate was used in program B. The HDS activities of the catalysts prepared from Ni–P(2) by program A and by program B are shown in Fig. 3. The final reduction temperature was 500 °C in both programs. It can be seen that keeping the temperature constant at 120 °C for 1 h markedly improved the HDS activities of the prepared phosphides. The improvement might be attributed to the removal of water retained on the surface of the catalysts before the reduction. Since the catalyst inevitably adsorbs some moisture during loading into the reactor, heating with high gas space velocity is a necessary step in the preparation of high-activity HDS catalysts in the in situ reduction method.

To clarify whether there is any reaction taking place when the temperature is kept at 120 °C, H_2 was replaced with N_2. As illustrated in Fig. 4, the gas type had little effect on the HDS performance of the prepared catalyst, indicating that sweeping with gas at 120 °C removes some adsorbents, which are detrimental to the formation of nickel phosphides, from the surface.

Fig. 5 shows the effect of the final reduction temperature on the HDS performance of the supported nickel phosphides prepared from Ni–P(2) by in situ reduction with program B. It is clear that the active phase can only be obtained above 400 °C, in accordance with results reported by Bussell and co-workers [18,23]. Therefore, it is suggested that reduction above 500 °C is necessary to prepare high-performance nickel phosphides.

The effect of the H_2 flow rate at 500 °C during reduction with program B on the performance of the prepared phosphides shows that a higher gas flow rate favors the formation of high-activity phosphides (Fig. 6). Stinner et al. [12] found that the flow rate of the reducing gas determines the type of nickel phosphide formed by reduction. H_2 flow rate changes influence the local partial pressures of volatile phosphorus species (intermediate reactant) and water (product) on the surface during reduction. An increase in gas flow rate leads to drops in the partial pressures of both phosphorus species

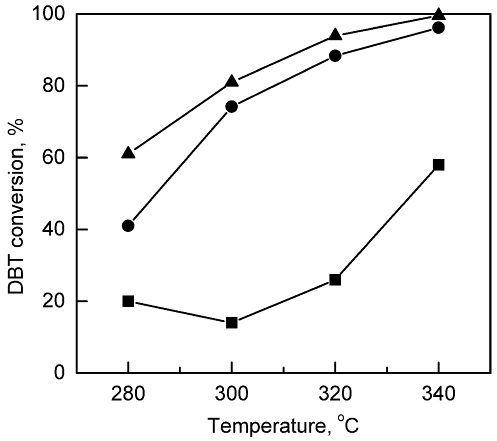

Fig. 7. HDS performance of Ni–P(2) supported on various carriers: (▲) MCM-41, (●) SiO_2, and (■) Al_2O_3.

and moisture locally on the surface. The drop in local partial pressure of phosphorus species has a negative effect on the reduction, and the decrease in local moisture has a positive effect. Therefore, the improvement in HDS activity can be attributed to the timely removal of water produced from the reduction reaction, suggesting that the removal of moisture from the surface during reduction is essential in the preparation of the supported nickel phosphides.

3.2. Preparation and properties of MCM-41-supported nickel phosphides

To further investigate catalyst preparation by the in situ reduction method, the effects of support, nickel loading, and Ni/P atomic ratio on the HDS activity of the obtained nickel phosphides were studied. The reduction program B (final reduction temperature 500 °C) and HDS reaction conditions were the same for each run. Fig. 7 shows the HDS performance of the catalysts prepared from Ni–P(2) precursors supported on alumina, silica, and siliceous MCM-41. The NiO loading was 20 wt%. The specific areas and pore volumes of the supported precursors are summarized in Table 2. Silica proved superior to alumina as the support for nickel phosphide catalysts. This observation was expected because there is a strong interaction between phosphorus species and alumina. It is assumed that silica and siliceous MCM-41 have similar surface properties because the pore wall of siliceous MCM-41 is amorphous silica. Nevertheless, a higher HDS performance was observed for the siliceous MCM-41-supported nickel phosphide. The improvement in HDS activity of the MCM-41-supported catalyst can be ascribed to its higher surface area (Table 2) and thus to the better dispersion of the phosphides.

The effect of the sum of the loadings of NiO and P_2O_5 on the HDS performance of the prepared nickel phosphides shows a maximum HDS performance at a loading of 20 wt% (Fig. 8). A high loading of P_2O_5 may block the pore channels during transformation of oxidic precursor to phosphides by the in situ reduction.

Table 2
Properties of catalyst precursors prepared from various supports

Catalyst precursor	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
Ni–P(2)/Al_2O_3	120	0.14
Ni–P(2)/SiO_2	206	0.44
Ni–P(2)/MCM-41	460	0.46

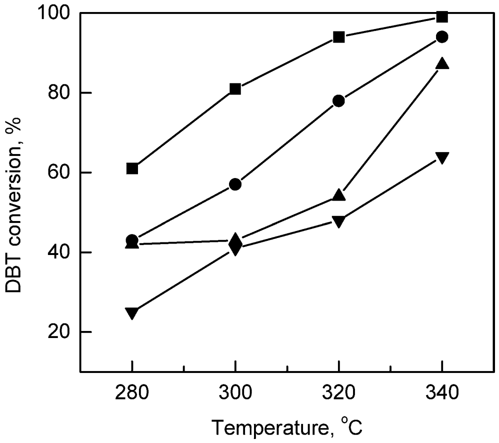

Fig. 8. Effect of the sum of the loadings of NiO and P_2O_5 on HDS performance of the prepared nickel phosphides for Ni–P(2): (▼) 10, (▲) 15, (■) 20, and (■) 25 wt%.

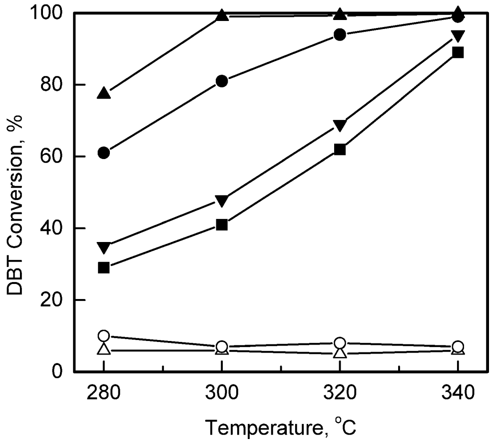

Fig. 9. HDS performance of the MCM-41-supported nickel phosphides prepared with various oxidic precursors with different Ni/P atomic ratios: (■) Ni–P(3), (●) Ni–P(2), (▲) Ni–P(1.25), (▼) Ni–P(1), (△) Ni–P(1/2), and (○) Ni–P(1/3).

Fig. 9 shows the HDS performance of various supported nickel phosphides prepared from precursors with different Ni/P ratios. When the Ni/P atomic ratio was above 1 in the precursor, the supported nickel phosphides exhibited a high HDS performance, and their reactivity increased with increasing reaction temperature. For the supported nickel phosphides with lower Ni/P atomic ratios, the HDS activity was quite low and hardly changed with reaction temperature. Oyama et al. [6,22] obtained a supported Ni_2P phase by starting with a precursor with a Ni/P atomic ratio of 1/2, and the supported Ni_2P showed a very high HDS activity.

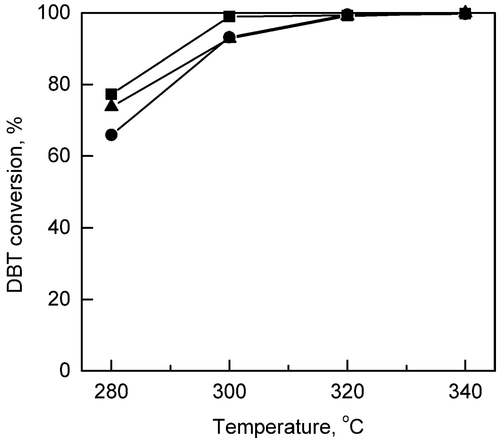

Fig. 10. Comparison of MCM-41-supported Ni_2P with Mo-base sulfides in HDS of DBT on a mass base: (■) Ni_2P, (▲) Ni–Mo(0.75) sulfides, and (●) Co–Mo(0.75) sulfides.

The difference between their results and ours may result from the H_2 reduction method. They used a low heating rate in the first reduction step of the traditional H_2 reduction, passivation, and rereduction method. The low heating rate allows the volatile phosphorus species to diffuse out of the pores easily, and the excess phosphorus is converted into gaseous products, while the remaining phosphorus guarantees the formation of the Ni_2P crystal structure. In the in situ reduction, a high heating rate is used, and a large quantity of excess volatile phosphorus species may be deposited and block the pores of the support. This also explains why the HDS activity hardly changed with reaction temperature for the catalyst prepared by the in situ reduction method. Among the MCM-41-supported nickel phosphides, a maximum HDS activity was observed for the one prepared from a precursor with a Ni/P atomic ratio of 1.25. Several researchers reported that nickel-rich phosphides are more active than phosphorus-rich phosphides. Among the nickel-rich phosphides, Ni_2P is the most active phase for HDS reaction. Nevertheless, an excess of phosphorus in the precursors was reported to be necessary for the preparation of silica-supported Ni_2P [12,18,22]. Our observation is consistent with the results reported for the traditional reduction–passivation–rereduction method.

An HDS activity comparison of Ni_2P/MCM-41 with the most active MCM-41-supported Mo-based sulfides [14,16] is shown in Fig. 10. It is indicated that all the three catalysts showed high activity in DBT HDS and that Ni_2P/MCM-41 exhibited activity equivalent to or higher than those of Ni–Mo or Co–Mo sulfides on a mass base, showing a great promise in deep HDS catalysis.

Since the reaction conditions for transformation of the oxidic precursor to the phosphide are similar to TPR characterization of the precursor, TPR profiles of the supported oxidic precursors may provide some insight into the reactions taking place during reduction. Fig. 11 presents the TPR profiles of the prepared MCM-41-supported oxidic precursors with various Ni/P atomic ratios, compared with MCM-41-supported NiO. Two main H_2 consumption peaks appeared at low temperatures in the profiles of the nickel-rich phosphides, whereas only one H_2 consumption peak was observed at high temperatures for phosphorus-rich phosphides. These observations are similar to the results reported by Oyama et al. [6]. Rodriguez et al. [23] recently studied the formation of nickel phosphides from a nickel-rich precursor by time-resolved X-ray diffraction. They found that the supported NiO was first reduced to Ni near 400 °C, which is in accordance with the TPR profile of NiO/MCM-41. However, the formation of nickel phosphides did not occur until the temperature reached 550 °C. Therefore, it is possible that the transformation of the oxidic precursor into phosphides starts with the reduction of NiO and that the formed Ni may assist the production of volatile phosphorus species and the formation of nickel phosphides. For the supported phosphorus-rich precursors, the excess phosphorus may hinder the reduction of NiO, and their TPR profiles resemble those of bulk precursors.

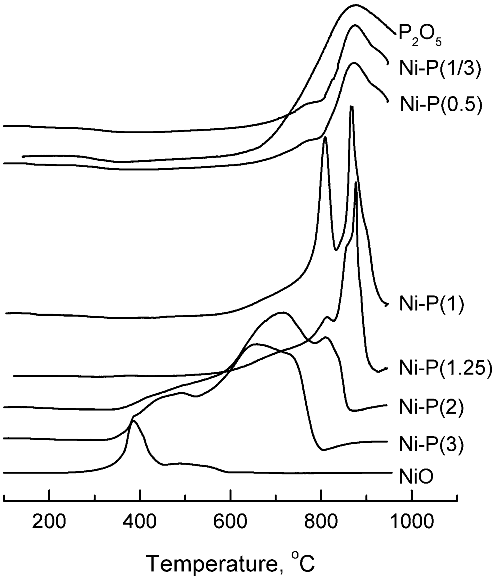

Fig. 11. TPR profiles of MCM-41-supported NiO, P_2O_5 and oxidic precursors of nickel phosphides with different Ni/P atomic ratios.

Stinner et al. [12] prepared silica-supported nickel phosphides and characterized the crystal phase of several nickel phosphides by XRD and ^{31}P NMR. They showed that ^{31}P NMR is an effective characterization method for supported and unsupported nickel phosphides. Figs. 12 and 13 show the ^{31}P NMR spectra measured for the MCM-41-supported nickel phosphides prepared from Ni–P(2) and Ni–P(1.25), respectively. The samples were prepared by in situ reduction, followed by passivation with 0.5% O_2 in Ar.

In the spectra of the supported nickel phosphides prepared from a precursor with a Ni/P ratio of 2, two sideband patterns were observed at three different spinning rates (Fig. 12). The chemical shifts were 1934 and 2262 ppm, which are typical of $Ni_{12}P_5$. Starting with a precursor with a stoichiometric Ni/P atomic ratio of 2, we actually obtained

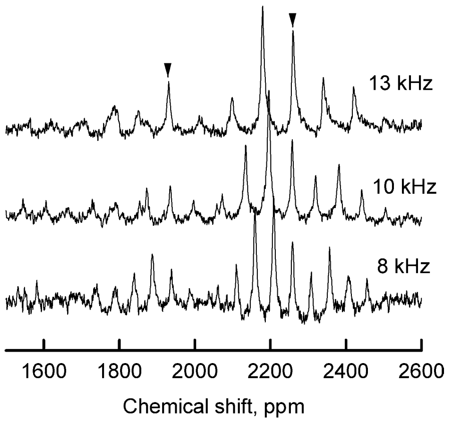

Fig. 12. ^{31}P MAS NMR spectra for MCM-41-supported nickel phosphide prepared from Ni–P(2)/MCM-41 at three different spinning rates.

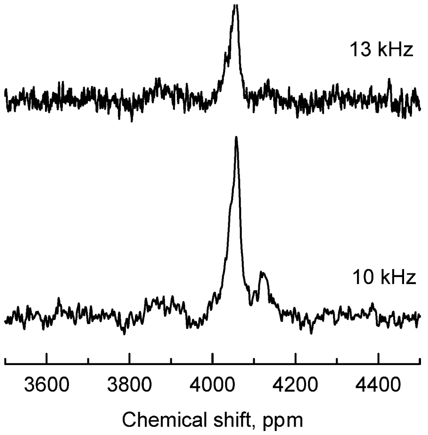

Fig. 13. ^{31}P MAS NMR spectra for MCM-41-supported nickel phosphide prepared from Ni–P(1.25)/MCM-41 at two different spinning rates.

supported $Ni_{12}P_5$. The HDS measurements showed that the supported $Ni_{12}P_5$ had a substantially high activity in HDS of DBT. Our results also confirmed that a precursor with a Ni/P atomic ratio of 2 did not yield supported Ni_2P by H_2 reduction. According to Rodriguez et al. [23], $Ni_{12}P_5$ is the reactant intermediate to Ni_2P, and more P might be needed to form Ni_2P.

Fig. 13 shows the ^{31}P NMR spectra of the supported nickel phosphides prepared from a precursor with a Ni/P atomic ratio of 1.25. An isotropic chemical shift of 4056 ppm, typical of Ni_2P, was observed. The XRD patterns also confirmed that the crystal phase was Ni_2P (Fig. 14). HDS activity evaluation revealed that siliceous MCM-41-supported Ni_2P was the most active structure among the prepared nickel phosphides, in accordance with the results for silica-supported nickel phosphides prepared by the traditional reduction–passivation–rereduction method [6].

4. Conclusions

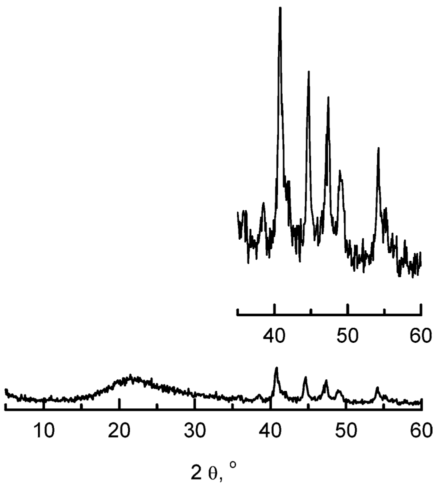

Fig. 14. XRD pattern of MCM-41-supported nickel phosphide prepared from Ni–P(1.25)/MCM-41.

An in situ reduction method was developed to transform nickel oxide precursors into supported nickel phosphides. The new method proved superior to the traditional reduction–passivation–rereduction method. A high heating rate and multistep programs are used in the in situ reduction. It seems that the removal of local moisture from the surface is crucial to the preparation of high-performance nickel phosphides.

Siliceous MCM-41 is superior to silica or alumina as a support for nickel phosphide HDS catalysts. Nickel-rich phosphides exhibited higher HDS activities than phosphorus-rich phosphides. Both $Ni_{12}P_5$ and Ni_2P are active in the HDS reactions; Ni_2P is the more active of the two. Ni_2P/MCM-41 exhibited higher HDS activity than MCM-41-supported Mo-based sulfides on a mass base. TPR characterization revealed that the transformation of oxidic precursor into nickel phosphides may start with the reduction of NiO to Ni, and that the formed Ni metal assists in the formation of nickel-rich phosphides.

Acknowledgments

The authors acknowledge financial support from the Natural Science Foundation of China (20003002, 20333030), the Education Ministry of China (20030141026), and the CNPC Innovation Foundation. We also thank Professor R. Prins for helpful discussions.

References

[1] T. Kabe, A. Ishihara, W. Qian, Hydrodesulfurization and Hydrodenitrogenation: Chemistry and Engineering, Wiley–VCH, Weinheim, 1999.
[2] C. Stinner, R. Prins, Th. Weber, J. Catal. 191 (2000) 438.
[3] P. Clark, X. Wang, S.T. Oyama, J. Catal. 207 (2002) 256.
[4] D.C. Phillips, S.J. Sawhill, R. Self, M.E. Bussell, J. Catal. 207 (2002) 266.
[5] X. Wang, P. Clark, S.T. Oyama, J. Catal. 208 (2002) 321.
[6] S.T. Oyama, X. Wang, Y.-K. Lee, K. Bando, F.G. Requejo, J. Catal. 210 (2002) 207.
[7] C. Stinner, R. Prins, Th. Weber, J. Catal. 202 (2001) 187.

[8] W.R.A.M. Robinson, J.N.M. van Gestel, T.I. Korányi, S. Eijsbouts, A.M. van der Kraan, J.A.R. van Veen, V.H.J. de Beer, J. Catal. 161 (1996) 539.
[9] T.I. Korányi, Appl. Catal. A: Gen. 239 (2003) 253.
[10] S.T. Oyama, J. Catal. 216 (2003) 343.
[11] P.J. Mangnus, J.A.R. van Veen, S. Eijsbouts, V.H.R. de Beer, J.A. Moulijn, Appl. Catal. 61 (1990) 99.
[12] C. Stinner, Z. Tang, M. Haouas, Th. Weber, R. Prins, J. Catal. 208 (2002) 456.
[13] R. Iwamoto, J. Grimblot, Adv. Catal. 44 (1999) 417.
[14] A. Wang, Y. Wang, T. Kabe, Y. Chen, A. Ishihara, W. Qian, J. Catal. 199 (2001) 19.
[15] A. Wang, X. Li, Y. Chen, D. Han, Y. Wang, Y. Hu, T. Kabe, Chem. Lett. (2001) 474.
[16] A. Wang, Y. Wang, T. Kabe, Y. Chen, A. Ishihara, W. Qian, P. Yao, J. Catal. 210 (2002) 319.
[17] A. Wang, T. Kabe, Chem. Commun. (1999) 2067.
[18] S.J. Sawhill, D.C. Phillips, M.E. Bussell, J. Catal. 215 (2003) 208.
[19] W. Qian, A. Ishihara, S. Ogawa, T. Kabe, J. Phys. Chem. 98 (1994) 907.
[20] S.T. Oyama, P. Clark, V.L.S. Teixeira da Silva, E.J. Lede, F.G. Requejo, J. Phys. Chem. B 105 (2001) 4961.
[21] Z. Wu, F. Sun, W. Wu, Z. Feng, Ch. Liang, Z. Wei, C. Li, J. Catal. 222 (2004) 41.
[22] S.T. Oyama, X. Wang, Y.-K. Lee, W.-J. Chun, J. Catal. 221 (2004) 263.
[23] J.A. Rodriguez, J.-Y. Kim, J.C. Hanson, S.J. Sawhill, M.E. Bussell, J. Phys. Chem. B 107 (2003) 6276.