1. Introduction

Emissions of SO\textsubscript{x} and NO\textsubscript{x} from automobile engines are one of the major sources of air pollution. SO\textsubscript{x} and NO\textsubscript{x} in the emissions are derived from the combustion of sulfur and nitrogen compounds present in fuels. Such sulfur species are also linked with particulate emissions, which are important in the formation of smog in the atmosphere. As a consequence, legislation requiring increasingly stringent limits on the contents of sulfur and nitrogen compounds in engine fuels has been introduced worldwide. The current government regulations in the US, Europe, and Japan limit the sulfur contents of diesel fuels to less than 10 ppm. The current regulation in China requires the sulfur content of diesel to reach 50 ppm, and new regulation which will further lower the sulfur limit to 10 ppm is scheduled to take effect by January 1, 2018. Unfortunately, the quality of crude oil has been decreasing, with higher sulfur and nitrogen contents. As a result, the production of ultra low sulfur- and nitrogen-content fuel by the hydrotreating process in a refinery has become increasingly challenging.

The active phases of industrial hydrotreating catalysts are Mo- or W-based sulfides with Ni or Co as the promoters. These sulfide catalysts exhibit substantially high activity and selectivity for removing most sulfur and nitrogen compounds in engine fuels made from crude oil. However, these catalysts are not active enough to remove “bulky” and refractory molecules like dibenzothiophene (DBT) and its derivatives, because DBT and its alkyl-substituted derivatives, such as 4-methyl dibenzothiophene (4-MDBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT), have extremely low activity in hydrodesulfurization (HDS). The HDS of DBTs proceeds in two parallel pathways: direct removal of sulfur by hydrogenolysis (DDS), and hydrogenation of aromatic rings followed by sulfur removal (HYD) (Fig. 1). The low HDS activity of DBTs is caused by the significant steric hindrance of the planar structure during vertical adsorption on the surface of the HDS catalysts. The substitution of alkyl groups at the 4 and 6 positions leads to dramatically increased steric hindrance. Therefore, sulfur in 4,6-DMDBT is very difficult to remove by the DDS pathway. On the other hand, the DBTs can also be horizontally adsorbed on the catalyst surface. The steric hindrance is markedly
decreased by hydrogenation of one or two of the aromatic rings in the DBTs, leading to significantly enhanced overall HDS activity. In other words, high hydrogenation activity is essential for the removal of refractory DBTs in the hydrotreating process. Therefore, new active phases with increased hydrogenation activity are highly desirable.

Precious metals are very active in hydrogenation, but are deactivated quickly in the presence of sulfur species. Metal carbides and metal nitrides exhibit much higher hydrogenation activity than metal sulfides, and show substantially higher initial HDS activity, but are slowly deactivated, probably due to the replacement of surface C and N with S during the HDS reactions. Similar to metal carbides and metal nitrides, metal phosphides combine the properties of metal and ceramics, and some metal-rich phosphides, such as Ni2P, MoP, WP, and CoP, are very active in HDS and hydrodenitrogenation (HDN)\(^2\)\(^{-4}\). Most importantly, these metal phosphides are stable against the sulfur species in HDS and HDN, so have great potential for hydrotreating catalysis (Table 1). In recent years, metal phosphides have attracted increasing attention in hydrodeoxygenation (HDO) catalysis\(^5\), because HDO is essential for upgrading renewable bio-ols to transportation fuels. Recent insightful articles have provided comprehensive reviews of the crystal structures, properties and catalytic performances in hydrotreating of metal phosphides\(^6\),\(^7\).

The present review will focus on the preparation, catalytic performance, and characterization of metal phosphides, mainly based on the research conducted in our group.

2. Preparation and Catalytic Performance of Metal Phosphides

The synthesis of metal sulfides is fairly straightforward, based on reaction of the oxide precursors with H\(_2\)S and sulfur compounds (even the sulfur-containing feed of a hydrotreating process) in a H\(_2\) flow at around 400 °C. In contrast, metal phosphides are complicated and difficult to synthesize. Metal phosphide can be prepared by reacting the metal with gaseous PH\(_3\)\(^8\), but PH\(_3\) is highly toxic and is not readily available commercially. Therefore, solid phosphorous sources, such as phosphate and phosphite, are frequently used for the preparation of supported metal phosphide catalysts. For example, MoP/MCM-41 is often prepared by temperature-programmed hydrogen reduction of oxide precursors which are obtained by impregnation, drying and calcination (Scheme 1). High temperature and high hydrogen flow rate are generally required for such reduction reactions to proceed. At elevated temperatures and in the presence of H\(_2\), the solid phosphorous sources are slowly converted into volatile P species (P and/or PH\(_3\)), which react with the metal and/or metal precursors to generate metal phosphide crystallites on the surface of the support. Consequently, the escape of volatile P species is inevitable in a H\(_2\) flow at high temperature. Therefore, excess P in the precursors is generally required\(^9\),\(^10\).

Like metal catalysts, freshly prepared metal phos-

| Table 1 Advantages and Disadvantages of Metal Phosphides, Metal Sulfides and Precious Metals as Hydrotreating Catalysts |
|---------------------------------------------------------------|
| Metal phosphides | Metal sulfides | Precious metals |
| Hydrogenation activity | high | low | high |
| HDS activity of 4,6-DMDBT | high | low | high |
| Sulfur tolerance | high | high | low |
| Preparation | difficult | easy | easy |
| Cost | low | low | high |

![Scheme 1 Procedure for Preparing MoP/MCM-41 Catalyst](image-url)
phides react vigorously with O2 in air. Consequently, the metal phosphides must be passivated with low concentration O2 gas after preparation to avoid excess oxidation and subsequent loss of structure during transferred through air. Since the oxide layer formed by passivation is not metallic and not active, re-reduction is a prerequisite for the use of passivated metal phosphides in hydrotreating reactions.

2.1. In-situ Reduction

The frequently used temperature-programmed reduction (TPR) method incorporates three stages, reduction, passivation, and re-reduction. To avoid the steps of passivation and re-reduction, and to preserve the surface structure, the in-situ reduction approach has been proposed (Scheme 1). Figure 2 compares the activities of Ni2P/MCM-41 prepared by reduction-passivation-reduction and by in-situ reduction in the HDS of DBT. The catalyst prepared by the in-situ reduction method was superior to that prepared by the reduction-passivation-reduction method. The higher activity of Ni2P/MCM-41 prepared by in-situ reduction might be attributable to the intact surface structure of Ni2P, which had not been exposed to air or O2. In the reduction-passivation-reduction approach, the passivation step leads to a slight loss of crystal structure, which cannot be restored by the subsequent re-reduction step. The in-situ reduction method is also more time-efficient, because the passivation and re-reduction stages are not needed.

2.2. H2 Plasma Reduction

Conversion of metal phosphates to metal phosphides by H2 reduction is not favored thermodynamically or kinetically. As a consequence, the forward reaction must be promoted by high temperatures and low vapor pressure of water (the by-product). As a result, metal phosphides are generally obtained by the TPR method at high temperature (>550 °C), low heating rate (e.g., 1 °C/min), and high H2 flow velocity.

Dielectric barrier discharge (DBD) plasma operates at ambient pressure and temperature in a non-equilibrium manner. The gap between the two electrodes leaves space for addition of the precursors. The non-equilibrium nature of the plasma is favorable to transform metal phosphates to metal phosphides. Moreover, the plasma-generated high-energy electrons collide inelastically with and transfer energy to the hydrogen molecules, leading to the formation of excited hydrogen species (H atom and excited H) and ions (mainly H3+). These species generated in H2 plasma are substantially more reactive than molecular hydrogen. Therefore, the oxide precursors can be converted into metal phosphides in the H2 plasma under very mild conditions (Scheme 1).

Figure 3 shows the development of Ni2P crystal phase in H2 plasma with time. The characteristic diffraction peaks of Ni2P were observable after 10 min, indicating that the plasma reduction method is much more time-efficient than the TPR method. Investigation of the reaction bed revealed that the reaction temperature was lower than 150 °C, which implies that the rapid reduction is attributable to the excited H species. Such low synthesis temperature also suppressed sintering of metal phosphide particles in supported catalysts, leading to increased dispersion of the active phase and resultant enhanced HDS performance.

Another advantage of the H2 plasma method is that metal phosphides are stoichiometrically synthesized, probably because of the high reactivity of excited H species and the low reaction temperature. In the TPR approach, part of the excess P in the precursors is lost from the reaction bed as volatile species (P and PH3) in the flowing H2 at high velocity and temperature. PH3 is highly toxic, and elemental P deposits in the downstream section of the reactor, so both escaping P species pose serious safety risks in large scale operations.

Figure 4A indicates that Ni3P and Ni2P were formed using Ni/P ratios of 2 and 3 in the precursors, respectively. Similarly, CoP and Co2P were formed using
Co/P ratios of 1 and 2 in the precursors (Fig. 4B). CoP was much less active than CoP in HDS. Therefore, careful control of the synthesis of CoP rather than Co2P or a mixture is essential in the preparation of CoP hydrotreating catalysts. Nevertheless, the synthesis of CoP requires harsher conditions than Ni2P, MoP, and WP. As a result, high performance CoP catalysts are extremely difficult to synthesize by the TPR method.

Figure 3B indicates that CoP could be synthesized stoichiometrically from the oxide precursors in H2 plasma.

The structural origin of the difference in activities of Ni2P catalysts prepared by the TPR and plasma reduction (PR) methods was investigated by identifying the chemical environments of Ni and P by X-ray absorption spectroscopy (XAS). XAS spectra at the Ni K-edge (8333 eV) of the MCM-41-supported Ni2P catalysts were recorded in the energy range 8233-9283 eV in a transmission mode at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility in China. The monochromator is equipped with a Si (111) channel-cut single crystal and has an energy range capability of 4000-22,000 eV. Extended X-ray absorption fine structure (EXAFS) data were processed and analyzed using the Athena (0.8.061) and Artemis (0.8.014) graphical interfaces to IFEFFIT.

Figure 5 shows the X-ray absorption near edge structure (XANES) spectra of Ni2P/MCM-41 prepared by the TPR and PR methods at the Ni K-edge. The intensity of the nickel white line peak at 8349 eV of Ni2P/MCM-41 (TPR) was higher than that of Ni2P/MCM-41 (PR). In general, the white line intensity in the Ni K-edge XANES spectra is a measure of the electron deficiency of Ni. The intensity of the pre-edge shoulder at 8334 eV of Ni2P/MCM-41 (PR) was lower. This shoulder is attributed to the 1s → 3d transition, which in perfect Oh symmetry is strictly dipole-forbidden, and the increase in absorbance usually corresponds to a decrease in oxidation state as well as a decrease in coordination number. This finding implies that Ni species in Ni2P/MCM-41 (TPR) were more electron deficient than those in Ni2P/MCM-41 (PR).

Due to the correlation effects in multishell fitting, only two-shell fitting analysis of the EXAFS oscillations was carried out without phase correction (Fig. 6). The EXAFS spectra of Ni2P/MCM-41 prepared by the
TPR and PR methods in $R$ space at $R \approx 0.3$ nm differed in two important aspects: peak intensity of the Ni–Ni shell for Ni$_2$P/MCM-41(TPR) was much lower, and Ni$_2$P/MCM-41(TPR) had a greater Ni–Ni bond length, indicating that the fine structures of the Ni$_2$P phases in the two catalysts were different. The curve-fitting results (Table 2) revealed that the structural parameters of the Ni$_2$P phase in Ni$_2$P/MCM-41(PR) were close to those of the reference, indicating a more perfect structure.

### 2.3. Sulfidation-reduction

Several experimental studies have shown that sulfur species are involved in HDS and HDN over metal phosphides$^{4,20}$, $^{23}$. Theoretical studies with density functional theory (DFT) of possible structures for the phosphosulfide overlayer on the Ni$_2$P(001) surface with H$_2$S adsorption and dissociation, as well as the replacement of surface phosphorus by sulfur, concluded that 50% of the surface phosphorus in the Ni$_2$P phase can be replaced by sulfur in hydrotreating reactions$^{24}$. All these results indicate that sulfur is involved in HDS or HDN in the typical hydrotreating process. Moreover, the incorporation of sulfur species on the surface of Ni$_2$P led to improved performance in HDS$^{25}$ and HDN$^{4}$. Therefore, we investigated the effect of sulfidation of the oxide precursors on the reduction and catalytic performances of synthesized metal phosphides in HDS of DBT and 4,6-DMDBT.

We started with the same oxide precursor used for the preparation of MoP/MCM-41 by the TPR method. In this new approach, the oxide precursor was sulfided at 400 °C for 3 h, and subsequently reduced by the TPR method at 400 to 650 °C and kept for 2 h (Scheme 1). XRD characterization and TEM observation revealed that the sulfidation caused a slight distortion of the MoP crystal structure prepared by the sulfidation-reduction method (MoP/MCM-41(SR)), compared with that by the conventional TPR method (MoP/MCM-41(R)). XPS analysis indicated that no S$^{2-}$ was present in MoP/MCM-41(R), indicating the presence of MoS$_2$ phase. Apparently the sulfur species were incorporated into the crystal structure of MoP, leading to the slight structural distortion.

Figure 7 compares the performance of MoP/MCM-41(SR) and MoP/MCM-41(R) for the HDS of DBT. Clearly MoP/MCM-41(SR) was more active than MoP/MCM-41(R). The improvement in HDS activity was attributed to the enhanced hydrogenation pathway (HYD), which occurs in parallel to the direct desulfurization pathway (DDS), in the HDS of DBT. In other words, MoP/MCM-41(SR) had superior hydrogenation activity compared to MoP/MCM-41(R) in the presence of sulfur-containing compounds.

As mentioned in the 1. Introduction, high hydrogenation rate is essential to efficiently remove sulfur in the bulky 4,6-DMDBT molecule, because of the significant steric hindrance induced by the methyl groups in the 4 and 6 positions. Therefore, we tested the performance of MoP/MCM-41(SR) for the HDS of 4,6-DMDBT, for comparison with MoP/MCM-41(R) (Fig. 8). MoP/MCM-41(SR) exhibited much higher HDS activity than MoP/MCM-41(R). Intriguingly, 4,6-DMDBT showed higher reactivity than DBT in the HDS reaction over MoP/MCM-41(SR) (Figs. 6 and 7), reversing the activity order in the HDS over other catalysts such as metal sulfides, noble metals, and Ni$_2$P.

In addition, WP/MCM-41 and Ni$_2$P/MCM-41 were also prepared by the sulfidation-reduction approach. Similarly, WP/MCM-41(SR) exhibited significantly higher activity than WP/MCM-41(R) for the HDS of DBT and 4,6-DMDBT. Moreover, 4,6-DMDBT was

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**Table 2** Curve-fitting Results of the Ni K-edge EXAFS Spectra for Ni$_2$P/MCM-41(TPR) and Ni$_2$P/MCM-41(PR)

| Ni-P shell | CN | $R$ [nm] | $\sigma^2 \times 10^{-4}$ [nm$^2$] | $\Delta E$ [eV] | Ni-Ni shell | CN | $R$ [nm] | $\sigma^2 \times 10^{-4}$ [nm$^2$] | $\Delta E$ [eV] | $R$-factor [%] |
|------------|----|---------|-------------------------------|----------------|-------------|----|---------|-------------------------------|----------------|----------------|
| Ni$_2$P reference | 2  | 0.2209  | 2  | 0.2605 | 2  | 0.2206  | 1.5 | 8.9 | 1.0 | 4.6 | 1.2 |
| Ni$_2$P/MCM-41(TPR)  | 4.2 | 0.2206  | 1.5 | −8.9 | 1.9 | 0.2210  | 0.9 | −4.8 | 1.6 | 0.2590 | 0.8 | 2.1 | 0.1 |
| Ni$_2$P/MCM-41(PR)  | 1.9 | 0.2210  | 0.9 | 1.0 | 1.6 | 0.2210  | 0.9 | 2.1 | 0.1 | 4.6 | 1.2 |

CN: coordination number; $R$: interatomic distance; $\sigma^2$: Debye-Waller factor; $\Delta E$: edge shift with respect to its theoretical position.

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**Fig. 7** HDS Conversion of DBT as a Function of Temperature over MCM-41-supported MoP Catalysts Prepared by Different Procedures: (■) MoP/MCM-41(SR), (○) MoP/MCM-41(R).
more easily desulfurized than DBT by HDS over WP/MCM-41(SR). Nevertheless, Ni$_2$P/MCM-41(SR) was less active than Ni$_2$P/MCM-41(R) for the HDS of DBT and 4,6-DMDBT. XRD characterization revealed that MoS$_2$ and WS$_2$ were readily converted to MoP and WP, respectively, by the subsequent reduction, whereas NiS was difficult to reduce.

**Figure 9** compares the catalytic activities of Ni$_2$P/MCM-41(R), MoP/MCM-41(SR), and WP/MCM-41(SR) for the simultaneous HDS of DBT and 4,6-DMDBT. 4,6-DMDBT was more reactive than DBT over MoP/MCM-41(SR) and WP/MCM-41(SR), confirming that MoP and WP catalyzes the HDS of 4,6-DMDBT more efficiently.

**Figure 10** illustrates the chromatograms of the product distributions from phenylethyne hydrogenation over Ni$_2$P/MCM-41(R), MoP/MCM-41(SR), and WP/MCM-41(SR). Both MoP/MCM-41(SR) and WP/MCM-41(SR) exhibited higher conversion than Ni$_2$P/MCM-41(R). Interestingly, MoP/MCM-41(SR) and WP/MCM-41(SR) showed substantially higher selectivity for aromatic ring saturation, even in the presence of styrene. High activity for the hydrogenation of aromatic rings is favorable to enhancement of the HYD pathway (Fig. 1). Due to the presence of the electron-donating methyl groups, 4,6-DMDBT adsorbs more strongly on the catalyst surface, and the aromatic rings are more easily hydrogenated. Since hydrogenation of aromatic rings is the rate-determining step in the HYD pathway, 4,6-DMDBT is more reactive than DBT in HDS over MoP and WP, which are much more active than Ni$_2$P for hydrogenation of aromatic rings. Apparently, HDS of 4,6-DMDBT over MoP/MCM-41(SR) and WP/MCM-41(SR) exhibited super hydrogenation activity even in the presence of sulfur compounds.

### 2.4. H$_2$S Passivation

Freshly prepared metal phosphides by H$_2$ reduction are extremely sensitive to air. Consequently, passivation, a process of mild oxidation on the surface of a metal phosphide to form a protective oxide layer, is needed before the metal phosphide is exposed to air. In the conventional passivation procedure, an inert gas containing a low concentration (0.5-1.0 %) of oxygen is frequently used. Since the protective oxide layer is inactive in HDS, it must be re-transformed to metal.
phosphide at high temperature in H₂ prior to HDS reactions. This reduction-passivation-reduction process is tedious and energy-intensive. Moreover, a slight loss of catalytic activity is often observed, probably because the re-reduction cannot completely restore the surface structure of the freshly prepared metal phosphide.

Incorporation of sulfur has been reported on the surface of metal phosphides, which involved favorable surface reconstruction, during HDS reactions. The theoretical calculation indicated that over 50% surface P can be replaced by S at ambient conditions. What if we replace O₂ with H₂S in the passivation? Figure 11 illustrates the performance of Ni₂P/MCM-41 catalysts passivated with O₂ and H₂S in HDS of DBT. H₂S-passivated Ni₂P/MCM-41 showed higher HDS activity than the O₂-passivated counterpart. Importantly, H₂S passivation does not require re-reduction prior to HDS reaction. Therefore, H₂S passivation is superior to O₂ passivation in the preparation of metal phosphides (Scheme 1).

Figure 12 shows the TEM images of bulk Ni₂P crystals which were passivated with H₂S (Fig. 12A) and O₂ (Fig. 12B), respectively. Amorphous phase was present on the O₂-passivated Ni₂P particles, whereas no such amorphous layer was present on the clear edge of the H₂S-passivated Ni₂P particles. Apparently O₂ passivation was more vigorous, leading to partial surface destruction of the Ni₂P particles. In contrast, H₂S passivation at room temperature was mild, and the crystal structure was well protected. H₂S-passivated Ni₂P/MCM-41 remained stable after storage in air for 150 d.

3. Summary

Metal phosphides can act as novel hydrotreating catalysts, with high HDS, HDN, and HDO activities. Intriguingly, MoP and WP prepared by the sulfidation-reduction method are excellent catalysts for the HDS of 4,6-DMDBT, which is a typical sulfur-containing molecule refractory to deep HDS. In contrast, 4,6-DMDBT has much lower reactivity than DBT over conventional metal sulfides catalysts. As a result, a catalyst bed of MoP or WP downstream of the conventional hydrotreating reactor may help to remove remaining DMDBTs in the hydrotreated diesel fractions, thus achieving ultradeep desulfurization. In addition, metal phosphides have been reported to show super catalytic performance in HDN and HDO in recent years. Therefore, metal phosphides are considered as promising hydrotreating catalysts in both petroleum-based refinery and biorefinery processes.

However, the preparation of metal phosphides is more challenging than that of conventional metal sulfides. Moreover, the catalytic performance of metal phosphides is history-dependent. As a result, research on metal phosphide hydrotreating catalysts has focused on easy and effective preparation. Due to the harsh preparation conditions (elevated temperatures), extremely small particles of metal phosphides are still difficult to prepare. Choice of low-valence phosphorous precursors, such as phosphites, hypophosphites, and pyrophosphates, could ameliorate the preparation conditions, allowing the formation of well-dispersed metal phosphides.

Another problem with supported metal phosphide catalysts is the interaction of P species with the support. Al₂O₃ is the most frequently used support in industrial applications. However, Al₂O₃ reacts with P species at high temperatures, making the P/metal ratio uncontrollable during preparation. Surface modification of Al₂O₃, solution synthesis of metal phosphides, and low-temperature synthesis of metal phosphides may be feasible methods for preparing Al₂O₃-supported metal phosphide catalysts.

Acknowledgment

This work was financially supported by NSFC (20503003, 20773020, 20973030, 21173033, U1162203), The Ph.D. Programs Foundation (MOE, 20100041110016), NCET (04-0275), and the “863”
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