

## Article

# High Active Zn/Mg-Modified Ni-P/Al<sub>2</sub>O<sub>3</sub> Catalysts Derived from ZnMgNiAl Layered Double Hydroxides for Hydrodesulfurization of Dibenzothiophene

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**Abstract:** A series of ZnMgNiAl layered double hydroxides (LDHs) containing 20 wt.% Ni and different Zn/Mg molar ratios were prepared by a coprecipitation method, and then were introduced with H<sub>2</sub>PO<sub>4</sub><sup>−</sup> via a microwave-hydrothermal method. With the resulting mixtures as the precursors, Zn/Mg-modified ZnMgNi-P/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared. The Zn/Mg molar ratio affected the formation of Ni<sub>2</sub>P and Ni<sub>12</sub>P<sub>5</sub> in nickel phosphides. The ZnMgNi-P/Al<sub>2</sub>O<sub>3</sub> catalyst with a Zn/Mg molar ratio of 3:1 exhibits the best dibenzothiophene hydrodesulfurization (HDS) activity. Compared with the Ni-P/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from the impregnation method, the ZnMgNi-P/Al<sub>2</sub>O<sub>3</sub> catalyst shows a higher HDS activity (81.6% vs. 54.3%) and promotes the direct desulfurization of dibenzothiophene.

**Keywords:** layered double hydroxides; nickel phosphide; microwave-hydrothermal treatment; hydrodesulfurization

## 1. Introduction

Sulfur removal has gained growing attention since the stringent fuel standards have been enacted throughout the world [1,2]. Among the existing sulfur removal methods, catalytic hydrodesulfurization (HDS) is a very efficient way to eliminate sulfur from fuel oil [3,4]. However, the existing commercial HDS catalysts fail to meet the regulated levels [5]. Studies on the hydrotreatment properties of metal phosphides show that nickel phosphide is the most promising candidate for the preparation of next-generation HDS catalysts [6–8].

Layered double hydroxides (LDHs,  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+} (A_{x/n}^{n-}) \cdot m\text{H}_2\text{O}$ ) are lamellarly-mixed hydroxides and a class of anionic clays having a hydrocalcite-like structure, which consist of positively charged mixed metal hydroxide layers and negatively charged interlayer anions [9]. LDHs have been demonstrated as effective precursors for the preparation of nickel phosphide catalysts. For instance, a Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from LDHs shows higher HDS activity than that prepared from the impregnation method, but the Ni loading up to 64.4 wt.% is unfavorable for the dispersion of active components [10].

The addition of other metals to LDH-derived catalysts contributes to HDS. For instance, the incorporation of Zn and Mg improved the catalytic activities for HDS. Chen et al. [11] found that Zn-doped NiAlMoW catalyst prepared from a NiZnAl-layered hydroxide precursor could improve 4,6-dimethyl dibenzothiophene HDS activity. The higher HDS activity is attributed to the promoter effect of Zn, since Zn decreases the interaction between alumina and active components (Ni, Mo, and W)

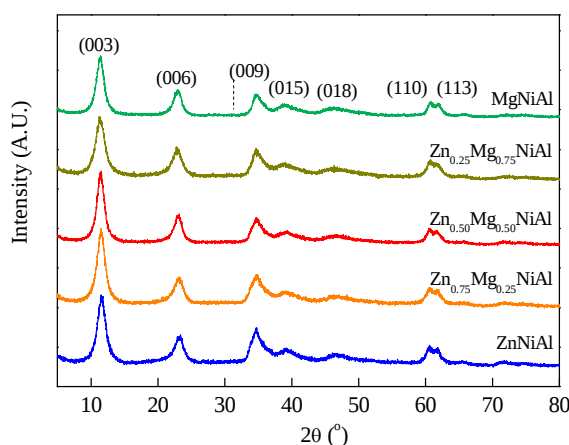
that forms Ni(Zn)–Mo(W)–S active species. CoMgMoAl catalysts derived from CoMgAl-terephthalate LDHs both enhanced the thiophene HDS and cyclohexene hydrogenation activities along with the increasing Mg content [12]. Nevertheless, research on development of a Zn/Mg-modified layered precursor for HDS is rare.

In the present work, a series of  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P/Al}_2\text{O}_3$  ( $x$  is the Zn/(Zn+Mg) molar fraction) catalysts were prepared by using  $\text{NH}_4\text{H}_2\text{PO}_4$  as the phosphorous precursor and  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  LDHs as the nickel precursor. In addition, the effects of Zn/Mg molar ratio on the structure and HDS performance of  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P/Al}_2\text{O}_3$  catalyst were investigated.

## 2. Results and Discussion

### 2.1. Characterization of Catalysts

Figure 1 shows the X-ray diffraction (XRD) patterns of  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  LDHs with different Zn/Mg molar ratios. Clearly, all the  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  LDHs show typical XRD patterns of LDHs, including a high intensity peak (003) at  $2\theta = 11.4\text{--}11.7^\circ$ , two weak peaks (006) and (009) at  $2\theta = 22.9\text{--}23.2^\circ$  and  $34.6\text{--}34.7^\circ$ , respectively, and two smaller peaks (110) and (113) of transition metal oxides at  $2\theta = 60\text{--}63^\circ$ . These results confirm the successful preparation of  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  LDHs [13]. No peaks of impurities were discerned, which indicates the high purity of the products.



**Figure 1.** X-ray diffraction (XRD) patterns of  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  layered double hydroxides (LDHs).

The structural parameters of  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  LDHs are listed in Table 1. The lattice parameters  $a$  and  $c$  are both almost the same among different  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  LDHs, despite the different Zn/Mg molar ratios. Then, the crystallite sizes at the  $a$ - and  $c$ -directions were calculated by the Scherrer formula based on the (110) and (003) reflections, respectively. It was found  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{NiAl}$  LDHs had much smaller crystallite size than the other catalysts.

**Table 1.** Analysis of XRD patterns for  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  LDHs.

| LDHs                                          | $d$ (nm) |       |       |       | Lattice Parameter <sup>1</sup> |      | Crystallite Size <sup>2</sup> |      |
|-----------------------------------------------|----------|-------|-------|-------|--------------------------------|------|-------------------------------|------|
|                                               | (003)    | (006) | (009) | (110) | $a$                            | $c$  | $a$                           | $c$  |
| ZnNiAl                                        | 0.76     | 0.38  | 0.26  | 0.15  | 0.30                           | 2.30 | 19.2                          | 9.2  |
| $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{NiAl}$ | 0.76     | 0.38  | 0.26  | 0.15  | 0.30                           | 2.30 | 14.1                          | 9.6  |
| $\text{Zn}_{0.50}\text{Mg}_{0.50}\text{NiAl}$ | 0.77     | 0.39  | 0.26  | 0.15  | 0.30                           | 2.33 | 20.6                          | 10.1 |
| $\text{Zn}_{0.25}\text{Mg}_{0.75}\text{NiAl}$ | 0.78     | 0.38  | 0.26  | 0.15  | 0.30                           | 2.32 | 20.5                          | 9.4  |
| MgNiAl                                        | 0.77     | 0.38  | 0.26  | 0.15  | 0.30                           | 2.31 | 16.0                          | 9.4  |

<sup>1</sup> Lattice parameters  $a = 2d_{110}$  and  $c = d_{003} + d_{006} + d_{009}$ , nm; <sup>2</sup> Crystallite sizes in direction  $a$  and  $c$ , nm.

The XRD patterns of  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$  are shown in Figure 2. Clearly,  $\text{ZnNi-P}/\text{Al}_2\text{O}_3$  shows the peaks at  $2\theta = 40.7^\circ$ ,  $44.6^\circ$ ,  $47.3^\circ$ , and  $54.1^\circ$  attributed to  $\text{Ni}_2\text{P}$ , and the typical peaks of  $\text{AlPO}_4$ ,  $\text{Zn}_3(\text{PO}_4)_2$ , and  $\text{Zn}_2\text{P}_2\text{O}_7$ . After the introduction of Mg, Ni still existed as  $\text{Ni}_2\text{P}$ , while the diffraction peaks of  $\text{Zn}_2\text{Mg}(\text{PO}_4)_2$  appeared at  $x = 0.75$  ( $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$ ). With a further increase of Mg dosage, in addition to the  $\text{Ni}_2\text{P}$ , the peaks of  $\text{Ni}_{12}\text{P}_5$  also appeared at  $2\theta = 47.0^\circ$  and  $49.0^\circ$  at  $x = 0.5$  ( $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Ni-P}/\text{Al}_2\text{O}_3$ ). At  $x = 0.25$  ( $\text{Zn}_{0.25}\text{Mg}_{0.75}\text{Ni-P}/\text{Al}_2\text{O}_3$ ), the diffraction peaks of  $\text{Ni}_2\text{P}$  are weakened until nearly invisible. For  $\text{MgNi-P}/\text{Al}_2\text{O}_3$ , Ni and Mg only existed as  $\text{Ni}_{12}\text{P}_5$  and  $\text{Mg}_3(\text{PO}_4)_2$ .

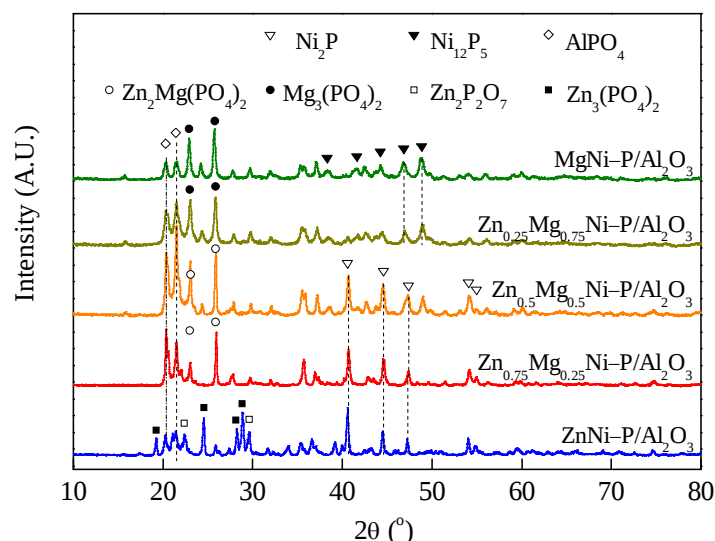


Figure 2. XRD patterns of  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$ .

Textural characteristics of typical catalysts are listed in Table 2. Clearly, all catalysts almost have the same pore volume. The  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$  has significantly higher specific surface area, but significantly smaller pore diameter and narrower pore size distribution (mainly concentrated in 2.3 nm) compared with  $\text{ZnNi-P}/\text{Al}_2\text{O}_3$  and  $\text{MgNi-P}/\text{Al}_2\text{O}_3$  (Figure 3a). Furthermore,  $\text{MgNi-P}/\text{Al}_2\text{O}_3$  shows typical IV  $\text{N}_2$  adsorption isotherms with obvious hysteresis loops at relative pressures between 0.43 and 0.95 (Figure 3b), which confirms the presence of mesopores.  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$  and  $\text{ZnNi-P}/\text{Al}_2\text{O}_3$ , however, show typical II  $\text{N}_2$  adsorption isotherms.

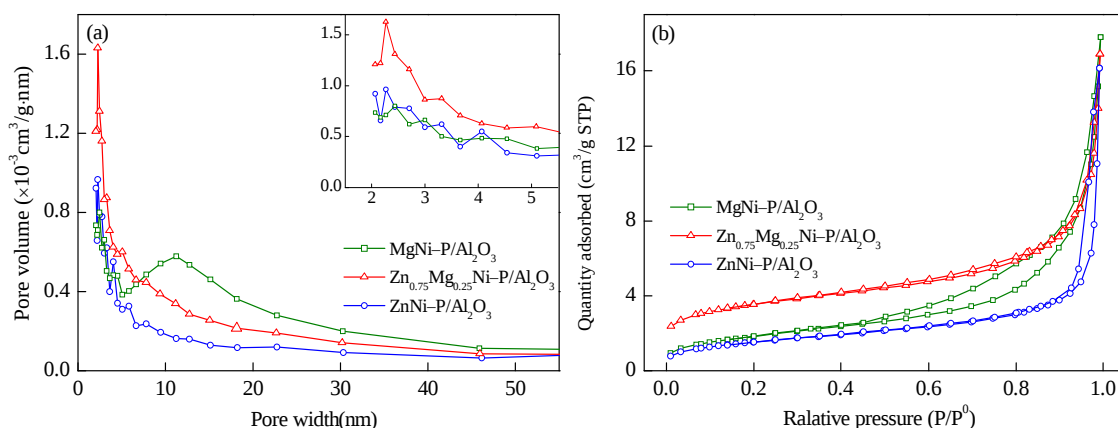
Table 2. Textural characteristics of  $\text{ZnNi-P}/\text{Al}_2\text{O}_3$ ,  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$ , and  $\text{MgNi-P}/\text{Al}_2\text{O}_3$ .

| Catalyst                                                            | Surface Area ( $\text{m}^2\cdot\text{g}^{-1}$ ) | Pore Volume ( $\text{cm}^3\cdot\text{g}^{-1}$ ) | Average Pore Diameter (nm) | $d_c$ <sup>1</sup> (nm) |
|---------------------------------------------------------------------|-------------------------------------------------|-------------------------------------------------|----------------------------|-------------------------|
| $\text{ZnNi-P}/\text{Al}_2\text{O}_3$                               | 5.5                                             | 0.025                                           | 18.2                       | 39.2                    |
| $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$ | 11.8                                            | 0.026                                           | 8.8                        | 29.4                    |
| $\text{MgNi-P}/\text{Al}_2\text{O}_3$                               | 6.7                                             | 0.027                                           | 16.5                       | —                       |

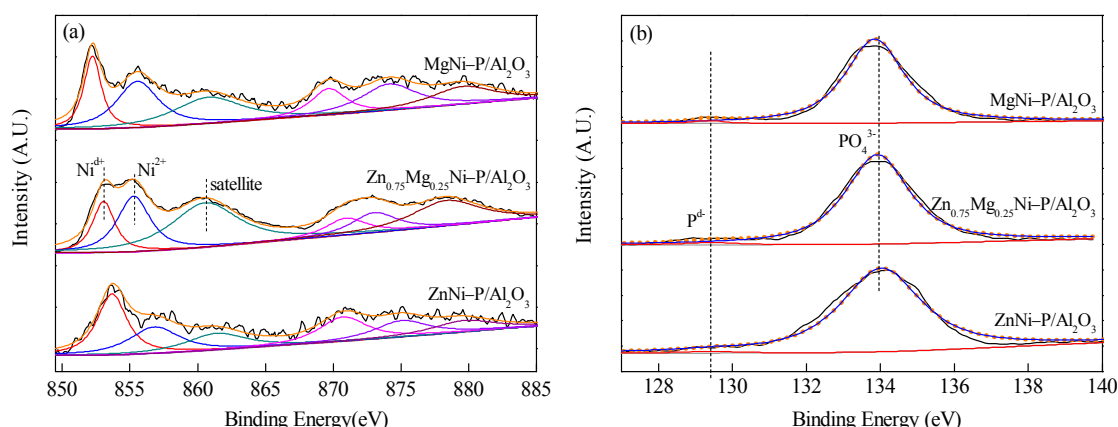
<sup>1</sup> Calculated from the  $d_c = K\lambda/\beta\cos(\theta)$  (Scherrer formula) based on the  $\text{Ni}_2\text{P}$  (111) ( $2\theta = 40.7^\circ$ ).

Figure 4 shows the X-ray photoelectron spectroscopy (XPS) spectra of  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$ , and the corresponding binding energies and surface composition are listed in Table 3. For  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$ , the peaks at 852.2–853.7 and 129.2–129.6 eV are assigned to  $\text{Ni}^{\delta+}$  ( $0 < \delta < 2$ ) and  $\text{P}^{\delta-}$  ( $0 < \delta < 1$ ) [14] (Figure 4a), respectively. The  $\text{Ni}^{\delta+}$  has higher binding energy than elemental Ni (852.5–852.9 eV), but lower than NiO (853.5–854.1 eV), indicating that the Ni in  $\text{Ni}_2\text{P}$  bears partial positive charge. The binding energy of  $\text{P}^{\delta-}$  is below the reported value of elemental P (Figure 4b).

In nickel phosphides, because of a covalent bond between the Ni and P atoms and a charge transfer from Ni to P, the electron-deficient Ni formed. Moreover, the peaks at 856.1–857.2 and 134.0–134.5 eV are assigned to  $\text{Ni}^{2+}$  and  $\text{P}^{5+}$  [7,15], respectively. In addition, a broad shake-up peak appears at the binding energy of  $\sim 5.0$  eV, which is higher than that of  $\text{Ni}^{2+}$  [16,17]. These peaks can be assigned to its satellite peaks, although they are located close to those of  $\text{Ni}^{3+}$  and nickel oxysulfide [18,19]. Moreover, the other broad peaks at higher binding energy are ascribed to the Ni 2p of nickel oxide [20].



**Figure 3.**  $\text{N}_2$  adsorption-desorption isotherms (a) and corresponding pore size distributions (b) for  $\text{ZnNi-P/Al}_2\text{O}_3$ ,  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P/Al}_2\text{O}_3$ , and  $\text{MgNi-P/Al}_2\text{O}_3$ .



**Figure 4.** XPS spectra of  $\text{ZnNi-P/Al}_2\text{O}_3$ ,  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P/Al}_2\text{O}_3$ , and  $\text{MgNi-P/Al}_2\text{O}_3$ : (a) Ni 2p; (b) P 2p.

**Table 3.** Spectral parameters obtained by X-ray photoelectron spectroscopy (XPS) analysis.

| Sample                                                       | Binding Energy (eV)  |                  |           |                     |                 | Surface Atomic Ratio  |      |                                                                                 |
|--------------------------------------------------------------|----------------------|------------------|-----------|---------------------|-----------------|-----------------------|------|---------------------------------------------------------------------------------|
|                                                              | Ni 2p <sub>3/2</sub> |                  |           | P 2p <sub>3/2</sub> |                 | Ni <sup>δ+</sup> /ΣNi | P/Ni | Surface Composition                                                             |
|                                                              | Ni <sup>δ+</sup>     | Ni <sup>2+</sup> | Satellite | P <sup>δ-</sup>     | P <sup>5+</sup> |                       |      |                                                                                 |
| $\text{ZnNi-P/Al}_2\text{O}_3$                               | 853.7                | 856.9            | 861.0     | 129.6               | 134.0           | 0.44                  | 7.41 | $\text{Zn}_{8.6}\text{Ni}_{5.9}\text{P}_{43.7}\text{Al}_{41.8}$                 |
| $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P/Al}_2\text{O}_3$ | 853.0                | 855.3            | 860.6     | 129.4               | 133.8           | 0.19                  | 1.87 | $\text{Zn}_{1.1}\text{Mg}_{9.2}\text{Ni}_{20.0}\text{P}_{37.4}\text{Al}_{32.3}$ |
| $\text{MgNi-P/Al}_2\text{O}_3$                               | 852.2                | 855.5            | 860.6     | 129.2               | 133.9           | 0.26                  | 4.42 | $\text{Mg}_{21.9}\text{Ni}_{9.9}\text{P}_{43.8}\text{Al}_{24.4}$                |

For  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P/Al}_2\text{O}_3$ , the interaction between the  $\text{Ni}_2\text{P}$  particles and the support leads to decrease of the binding energy of  $\text{Ni}^{\delta+}$  (853.1 eV) [10,21]. As reported, the hydrogenation ability of the Ni site reduces with the decrease of electron density [22,23]. For  $\text{MgNi-P/Al}_2\text{O}_3$ , the binding energy of  $\text{Ni}^{\delta+}$  in  $\text{Ni}_{12}\text{P}_5$  phase declines further (852.2 eV). Compared with  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P/Al}_2\text{O}_3$ ,

the binding energy of  $\text{Ni}^{\delta+}$  in  $\text{MgNi-P}/\text{Al}_2\text{O}_3$  is further reduced, indicating that less electron density is transferred from Ni to P in  $\text{Ni}_{12}\text{P}_5$  compared with  $\text{Ni}_2\text{P}$ . Sawhill et al. [15] also reported that the Ni in  $\text{Ni}_{12}\text{P}_5$  has a higher electronic density than  $\text{Ni}_2\text{P}$ .

The superficial atomic ratios of the catalysts were determined by XPS and the results are listed in Table 3. As shown from these results, the P/Ni molar ratio determined from the surface composition is far larger than the stoichiometric ratio of  $\text{Ni}_2\text{P}$  or  $\text{Ni}_{12}\text{P}_5$ , which confirms the occurrence of surface P enrichment in the catalysts. Nonetheless, the  $\text{Ni}^{\delta+}/\Sigma\text{Ni}$  ratio is lower than 1 for all the catalysts, which indicates the presence of a large proportion of nickel oxide. The phosphorus on the catalyst surfaces essentially exists as  $\text{PO}_4^{3-}$ . In addition, the P/Ni molar ratio is the lowest in  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$ , which indicates that more Ni sites on the catalyst surface are exposed under the same Ni loading.

XRD of  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$  (Figure 2) shows that Ni, Zn, and Mg all could react with P, thereby affecting the formation of  $\text{Ni}_2\text{P}$  and  $\text{Ni}_{12}\text{P}_5$ . Thus, how the single loading of ZnO or MgO would affect the formation of  $\text{Ni}_2\text{P}$  and  $\text{Ni}_{12}\text{P}_5$  was further studied. The XRD patterns of different nickel phosphate catalysts are shown in Figure 5. For  $\text{Ni-P}/\text{Al}_2\text{O}_3$ , Ni and P only exist as  $\text{Ni}_2\text{P}$ , without any other phase, indicating that the active phase is  $\text{Ni}_2\text{P}$ . For  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$  and  $\text{Ni-P}/\text{ZnO}$ , Ni and P mainly exist as  $\text{Ni}_2\text{P}$ , accompanied by a small amount of  $\text{AlPO}_4$  and  $\text{Zn}_3(\text{PO}_4)_2$ , respectively. For  $\text{Ni-P}/\text{MgO}$ , Ni, P and Mg exist as  $\text{MgNiO}_2$  and  $\text{Mg}_3(\text{PO}_4)_2$ .

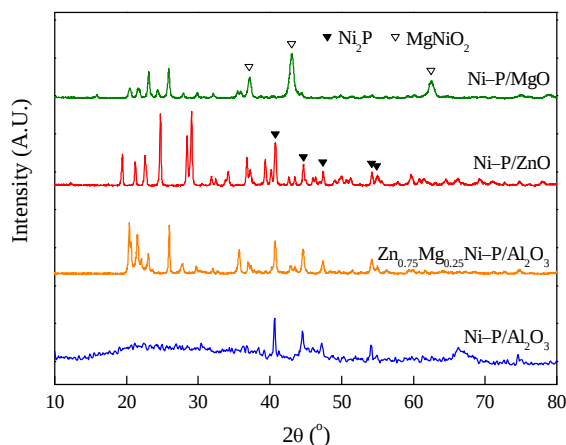
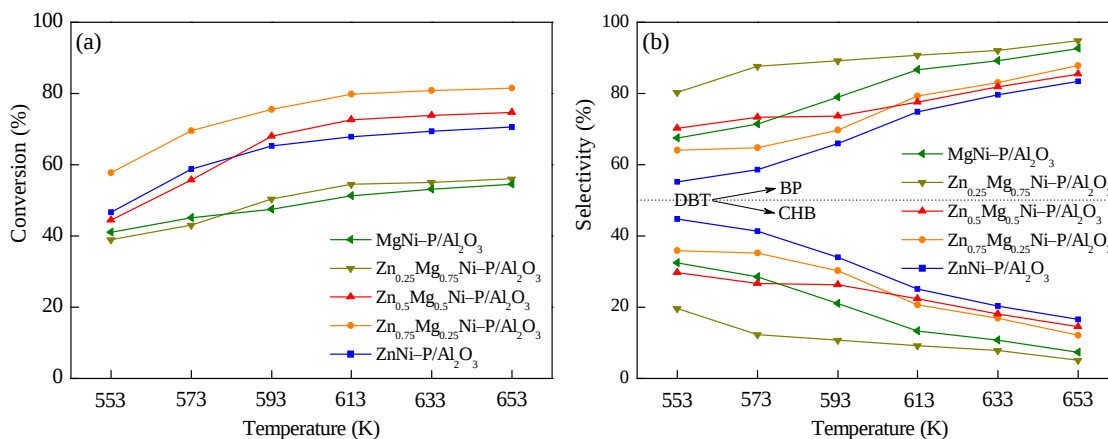


Figure 5. The XRD patterns of different nickel phosphate catalysts.

## 2.2. Catalytic Activity

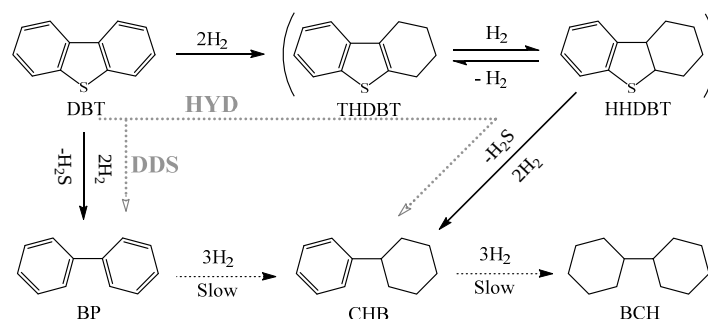
Figure 6 shows the HDS of dibenzothiophene (DBT) over  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$  at varying temperatures. Clearly, the DBT conversion increases with the increase in temperature for all the catalysts (Figure 6a). The DBT conversion is promoted slowly with a further temperature rise above 613 K. Moreover, with the increase of Mg content, the DBT conversion over  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$  first increases and then decreases compared with  $\text{ZnNi-P}/\text{Al}_2\text{O}_3$ . At the reaction temperature of 653 K, and at the Zn/Mg molar ratio of 3:1 (i.e.,  $x = 0.75$ ), the DBT conversion over  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$  is maximized to 81.6%, and under the same conditions the conversion rates of  $\text{ZnNi-P}/\text{Al}_2\text{O}_3$  and  $\text{MgNi-P}/\text{Al}_2\text{O}_3$  are 70.6% and 54.6%, respectively. From the perspective of active phase composition, for  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$ , XRD shows the nickel phosphide exists as  $\text{Ni}_2\text{P}$  at  $x \geq 0.75$ ; the composition at  $x = 0.5$  is mainly  $\text{Ni}_2\text{P}$  and a small amount of  $\text{Ni}_{12}\text{P}_5$ ; the composition at  $x = 0.25$  is mainly  $\text{Ni}_{12}\text{P}_5$  and a small amount of  $\text{Ni}_2\text{P}$ ; at  $x = 0$ , only  $\text{Ni}_{12}\text{P}_5$  exists (Figure 2). For nickel phosphides,  $\text{Ni}_2\text{P}$  shows much higher hydrogenation activity than  $\text{Ni}_{12}\text{P}_5$  [6]. In addition, the HDS reaction mainly occurs on metal sites. From the perspectives of active phase composition/distribution and active particle size, XPS shows that more nickel sites are exposed on the surfaces of  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$  compared with  $\text{ZnNi-P}/\text{Al}_2\text{O}_3$  (Table 3). The particle sizes of  $\text{Ni}_2\text{P}$  in  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$  and  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Ni-P}/\text{Al}_2\text{O}_3$  calculated by the Scherrer formula are 29.4 and 34.8 nm, respectively.

The smaller sizes of active  $\text{Ni}_2\text{P}$  particles could promote the dispersion of the active  $\text{Ni}_2\text{P}$  phase as well as the active specific surface area. Furthermore, compared with  $\text{ZnNi-P}/\text{Al}_2\text{O}_3$  and  $\text{MgNi-P}/\text{Al}_2\text{O}_3$  modified by a single metal, the modification by double metals ( $\text{Zn}+\text{Mg}$ ) could reduce the mesoporous size and increase the micropore amount of  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$ .



**Figure 6.** Evolution of conversion (a) and selectivity (b) of dibenzothiophene (DBT) hydrodesulfurization (HDS) over  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$  catalysts,  $P = 3 \text{ MPa}$ , weight hourly space velocities (WHSV) =  $2.0 \text{ h}^{-1}$  and  $\text{H}_2/\text{oil}$  ratio =  $500 \text{ (V/V)}$ .

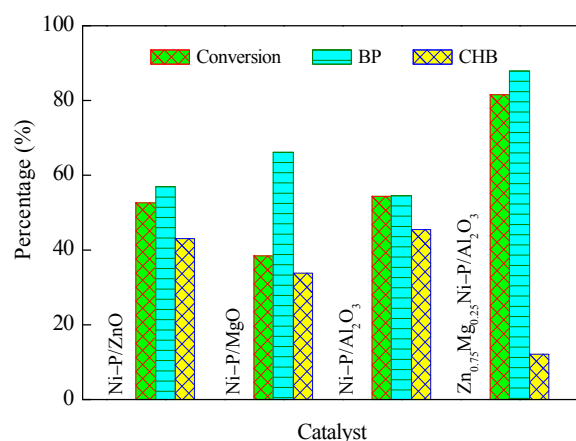
The reaction scheme for the HDS of DBT is presented in Scheme 1. The HDS of DBT occurs via direct desulfurization (DDS) and hydrogenation (HYD), which mainly form biphenyl (BP) and cyclohexylbenzene (CHB), respectively. The BP formed during DDS would undergo slow hydrogenation to form CHB, while the intermediates tetrahydrodibenzothiophene (THDBT) and hexahydrodibenzothiophene (HHDBT) formed during HYD were hydrogenated to CHB, which was further hydrogenation to bicyclohexyl (BCH). It was found that the HDS products of DBT on  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$  are only BP and CHB. Similar product distributions have been reported [24–26]. As showed in Figure 6b, the selectivity of BP increases and that of CHB decreases with the increase in temperature for all catalysts. The proportions of BP are larger over all the samples, indicating that DBT is mainly desulfurized via the DDS pathway. This conclusion agrees with Song et al. [10] who prepared  $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$  catalysts from  $\text{Ni-Al-CO}_3^{2-}$  LDHs. Interestingly, the selectivity of BP over  $\text{Ni}_{12}\text{P}_5$  is higher than that of  $\text{Ni}_2\text{P}$  for  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$ , which indicates that  $\text{Ni}_{12}\text{P}_5$  is more active in DDS than  $\text{Ni}_2\text{P}$ .



**Scheme 1.** Simplified reaction pathways for the HDS of DBT.

For comparison, the HDS of DBT over different catalysts is shown in Figure 7. The HDS activities of the catalysts change in the order of  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3 > \text{Ni-P}/\text{Al}_2\text{O}_3 > \text{Ni-P}/\text{ZnO} > \text{Ni-P}/\text{MgO}$ . Compared with the widely-studied  $\text{Ni-P}/\text{Al}_2\text{O}_3$ ,  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$  enhances not only HDS

activity (from 54.3% to 81.6%), but also the selectivity of BP (from 54.6% to 87.8%) and the DDS pathway. XRD shows that the active phase is  $\text{Ni}_2\text{P}$  and not  $\text{Ni}_{12}\text{P}_5$  for both  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$  and  $\text{Ni-P}/\text{Al}_2\text{O}_3$  (Figure 2). As reported,  $\text{Ni}_2\text{P}$  has two types of sites, including tetrahedral Ni(1) sites and square pyramidal Ni(2) sites, which are responsible for HDS by the DDS route and desulfurization by the HYD route, respectively [27]. Therefore,  $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Ni-P}/\text{Al}_2\text{O}_3$  prepared from LDHs enhances the Ni(1) sites compared with  $\text{Ni-P}/\text{Al}_2\text{O}_3$ . The HDS activity of  $\text{Ni-P}/\text{MgO}$  is the lowest, because the preferential reactions between P and Mg inhibits the formation of  $\text{Ni}_2\text{P}$  and  $\text{Ni}_{12}\text{P}_5$ .



**Figure 7.** HDS of DBT over different catalysts,  $T = 653\text{ K}$ ,  $P = 3\text{ MPa}$ ,  $\text{WHSV} = 2.0\text{ h}^{-1}$  and  $\text{H}_2/\text{oil}$  ratio = 500 (V/V).

### 3. Experimental

#### 3.1. Materials

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were purchased from Beijing Shuanghuan Chemical Reagents Company (Beijing, China). NaOH was provided by Tianjin Yongda Chemical Reagent Co., Ltd. (Tianjin, China).  $\text{Na}_2\text{CO}_3$  was supplied by Tianjin Damao Reagents Company (Tianjin, China).  $\text{HNO}_3$  was obtained from Haerbin Chemical Reagent Company (Haerbin, China).  $\text{NH}_4\text{H}_2\text{PO}_4$  was purchased from Beijing Chemical Company (Beijing, China). A model oil was prepared by  $\text{C}_{12}\text{H}_8\text{S}$  (AccuStandard Inc., New Haven, CT, USA),  $\text{C}_{10}\text{H}_{18}$  (Beijing Chemical Company, Beijing, China), and  $\text{C}_{14}\text{H}_{30}$  (Tianjin North Chemical Reagents Company, Tianjin, China). All the chemicals were of analytical grade and used with no further treatment. Deionized water was used for solution preparation.

#### 3.2. Catalyst Preparation

A series of  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  LDHs with  $\text{M}^{2+}/\text{M}^{3+}$  molar ratio of 3:1 and different Zn/Mg molar ratios were prepared from coprecipitation under ambient atmosphere. Each time, a mixed solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was adjusted to pH 10 by adding a NaOH and  $\text{Na}_2\text{CO}_3$  aqueous solution dropwise under stirring. The resulting suspension was aged at 333 K for 6 h. The precipitate was filtered and washed several times with deionized water. Then,  $\text{Zn}_x\text{Mg}_{1-x}\text{Ni-P}/\text{Al}_2\text{O}_3$  catalysts were prepared by a microwave-hydrothermal treatment and temperature programmed reduction, as described in our previous work [10]. Typically,  $\text{Zn}_x\text{Mg}_{1-x}\text{NiAl}$  LDHs were impregnated with an ammonium dihydrogenphosphate solution with a Ni/P molar ratio of 1:2 and treated using a microwave-hydrothermal method for 20 min at 363 K under reflux. After drying at 393 K for 12 h, the resulting materials were pressed into discs, crushed, and sieved to particles with 16–30 meshes. After calcination at 773 K for 3 h, the materials were reduced in a  $\text{H}_2$  flow (200 mL/min) while the temperature rose to 973 K at a rate of 2 K/min and was then maintained at

973 K for 2 h. Then, the materials were cooled to room temperature in a H<sub>2</sub> flow, and passivated in a 20 mL/min O<sub>2</sub>/N<sub>2</sub> flow (0.5 vol.% O<sub>2</sub>).

For comparison, Ni-P/Al<sub>2</sub>O<sub>3</sub> (Ni-P/ZnO and Ni-P/MgO) catalyst was prepared by dissolving a Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) mixed solution in HNO<sub>3</sub>. After evaporation, the resulting solids were calcined, and reduced by heating to 873 K at a rate of 2 K/min in a H<sub>2</sub> flow. The Ni/P molar ratio and theoretical Ni loading were 1:2 and 20 wt.%, respectively, for all catalysts.

### 3.3. Catalyst Characterization

XRD patterns were measured on a Rigaku D/max-2200 X-ray diffractometer operated at 40 kV and 40 mA using Cu K $\alpha$  radiation. The textural properties of the catalysts were analyzed by the Brunauer-Emmett-Teller (BET) method using a Tristar II3020 surface area and porosity analyzer. XPS spectra were acquired with a K-Alpha electron spectrometer (ThermoFisher Scientific Company, Waltham, MA, USA) using an Al K $\alpha$  radiation source (1486.6 eV). The binding energy was calibrated by setting the C1s transition at 284.8 eV.

### 3.4. Catalytic Hydrogenation Activity Test

The HDS reaction of DBT was performed on a fixed-bed reactor [10]. Prior to the reaction, 0.65 g of a passivated catalyst was activated in H<sub>2</sub> (40 mL/min) at 773 K for 2 h. After activation, the hydrotreatment reaction was carried out at 553 K, 3.0 MPa. The liquid reactant, which consisted of a decalin solution of DBT (1 wt.%), was pumped into the reactor. The weight hourly space velocities (WHSV) and H<sub>2</sub>/oil ratio (V/V) were 2.0 h<sup>-1</sup> and 500, respectively. Liquid product compositions of the samples collected at a 2-h interval were determined on a GC-14C gas chromatograph equipped with a SE-30 capillary column.

## 4. Conclusions

Zn/Mg-modified Zn<sub>x</sub>Mg<sub>1-x</sub>NiAl LDHs with different Zn/Mg molar ratios were prepared. Briefly, H<sub>2</sub>PO<sub>4</sub><sup>2-</sup> was introduced by the microwave-hydrothermal method, and Zn<sub>x</sub>Mg<sub>1-x</sub>Ni-P/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared with the mixture as the precursor. In the precursors, under the hydrogenation atmosphere and during temperature programmed reduction, both Zn and Mg reacted with phosphorus substances, which impacted the formation of nickel phosphates. The nickel phosphate mainly existed in the form of Ni<sub>2</sub>P at  $x \geq 0.5$ , but Ni<sub>12</sub>P<sub>5</sub> at  $x < 0.5$ . Compared with the single-metal-modified catalysts (Zn or Mg), the Zn/Mg-modified (Zn/Mg molar ratio of 3:1) Zn<sub>0.75</sub>Mg<sub>0.25</sub>Ni-P/Al<sub>2</sub>O<sub>3</sub> effectively reduced the pore sizes of catalysts, increased the pore counts, and had the smallest Ni<sub>2</sub>P particles. The catalyst prepared from this method showed the highest dibenzothiophene hydrodesulfurization activity and promoted the direct desulfurization of dibenzothiophene.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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