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硫化镍和磷化镍的 HDS 加氢活性和稳定性

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摘要：采用共沉淀法制备了高分散 80%Ni/Al_2O_3 催化剂，经 350 ℃焙烧，得高分散 NiO/Al_2O_3(NiO 粒径 ~3 nm)，将其以 CS_2 硫化(310 ℃, 4 h) 或 PPh_3 磷化(320 ℃, 36 h)，分别获得了高分散的硫化镍(Ni_3S_2 和 Ni_3S_4, 5.8 nm) 和 Ni_2P(7.0 nm)，在二苯并噻吩(DBT) 的加氢脱硫(HDS) 反应中，Ni_2P 的活性远高于 NiS_x(360 ℃时 DBT 的转化率分别为 100% 和 75%). 若将 NiS_x 用 PPh_3 磷化，则 NiS_x 全部转化为 Ni_2P(13.3 nm)，其 HDS 活性远高于原来的 NiS_x 且与直接磷化获得的 Ni_2P(7.0 nm) 相当. 反之，若将 Ni_2P 用 CS_2 硫化，则 Ni_2P 物相不变，粒径也没有长大，表明 Ni_2P 物相远比 NiS_x 稳定，且其 HDS 活性高于直接磷化的 Ni_2P，表明其 Ni_2P 表面可能生成了 HDS 活性更高的某种 Ni-P-S 物种.

关键词：Ni_2P/Al_2O_3 催化剂；NiS_x/Al_2O_3 催化剂；PPh_3 液相磷化；CS_2 液相硫化；物相稳定性；加氢精制反应
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硫化镍本身在加氢精制反应中的加氢脱硫(HDS) 活性并不理想，主要作为硫化钼或钨体系的助催化剂，组成 γ-Al_2O_3 或 SiO_2 担载的 Ni-Mo-S 和 Ni-W-S 催化剂. 磷化镍具有较高的 HDS、加氢脱氮(HDN) 活性和较高的耐硫性能，有可能替代传统的过渡金属硫化物催化剂用于加氢精制反应. 文献中关于硫化镍和磷化镍的比较研究很少. 由于原料和制备方法对催化剂的组成和性能影响很大，比较硫化镍和磷化镍并非易事.

我们采用共沉淀法制备了高担载量和高分散度的 80%Ni/Al_2O_3 催化剂，经 350 ℃焙烧后获得了高分散的 NiO/Al_2O_3 催化剂前驱体，其中 NiO 的粒径约为 3 nm. 用 CS_2 在 310 ℃将 NiO/Al_2O_3 硫化 4 h，获得了高分散的硫化镍(Ni_3S_2 和 Ni_3S_4)，粒径约为 5.8 nm. 用三苯基膦(PPh_3) 将上述硫化镍磷化，如果磷化温度较低(170~220 ℃)，硫化镍就无法被磷化，但其粒径会逐渐增大至 8.4 nm. 在 270 ℃时部分硫化镍已被磷化成 Ni_2P，粒径增大至 11.7 nm. 磷化温度升至 320 ℃，硫化镍全部转化为 Ni_2P，得到 NiS_x (P)$/Al_2O_3$ 催化剂，Ni_2P 粒径也进一步增大到 13.3 nm.

如果将所得的 Ni/Al_2O_3 用 PPh_3 在 320 ℃磷化 36 h，NiO 就转化为纯 Ni_2P 物相(粒径约为 7.0 nm)，得到 Ni_2P/Al_2O_3 催化剂. 用 CS_2 硫化 Ni_2P/Al_2O_3 时，即使温度提高到 360 ℃，催化剂中仍只检测到 Ni_2P 物相，表明 Ni_2P 物相比硫化镍(Ni_3S_2 和 Ni_3S_4) 物相更加稳定，难以被 CS_2 硫化，这是 Ni_2P 具有较高耐硫性能的重要原因. 硫化后的 Ni_2P (S)$/Al_2O_3$ 催化剂中 Ni_2P 粒径增大到 9.5 nm，但仍比 320 ℃磷化硫化镍得到的 Ni_2P 的粒径(13.3 nm) 小得多，证明 Ni_2P 物相和粒径都比较稳定.

分析催化剂的化学组成发现，硫化镍经 PPh_3 磷化后仅剩余了 3% 的 S，即绝大部分 S 已被 P 取代，NiS_x 转化成了 Ni_2P，而磷化镍经 CS_2 硫化后只有 1.1% 的 S 进入催化剂中，且未检测到硫化物物相，表明 Ni_2P 确实具有很强的抗硫性能. 此外，无论是将硫化镍磷化，还是将磷化镍硫化，所得样品中 P/Ni 比值相似(0.74)，均高于 Ni_2P 的化学计量比 0.5，说明除了 Ni_2P 外，催化剂中还可能存在富磷磷化镍或其他含 P 物种.

将上述直接磷化或硫化得到的 Ni_2P/Al_2O_3 和 NiS_x/Al_2O_3 催化剂，以及硫化镍再磷化(NiS_x (P)$/Al_2O_3$) 和磷化镍再硫化(Ni_2P (S)$/Al_2O_3$) 后的催化剂分别用于模型柴油(含 1.72% (质量分数) 的二苯并噻吩(DBT)、0.185% (质量分数) 的喹啉、5% (质量分数) 的四氢萘) 的加氢精制反应. 反应后，Ni_2P/

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Al_2O_3 和 NiS_x/Al_2O_3 催化剂的物相都没有发生变化，表明 Ni_2P 和 NiS_x 物相在加氢精制反应过程中均是稳定的. NiS_x（P）/Al_2O_3 经过 HDS 反应，Ni_2P 的 XRD 衍射峰依然存在，且较强，表明该催化剂在反应条件下没有被 DBT 硫化，即由硫化镍磷化而转化来的 Ni_2P 在加氢精制反应条件下也是稳定的. Ni_2P（S）/Al_2O_3 经过 HDS 反应，仍以 Ni_2P 物相为主，但出现了 NiP_2，可能是因为催化剂中残留了过量 P，它在温度较高时与 Ni_2P 反应，生成了过磷化物 NiP_2.

在 DBT 的 HDS 反应中，Ni_2P/Al_2O_3 的 HDS 活性远高于 NiS_x/Al_2O_3. 在 360 ℃时，以 Ni_2P 为主要物相的 Ni_2P/Al_2O_3、NiS_x（P）/Al_2O_3 和 Ni_2P（S）/Al_2O_3 的 DBT 加氢脱硫活性均达到了 100%，而 NiS_x/Al_2O_3 的 DBT 转化率只有 75%. 同时，Ni_2P（S）/Al_2O_3 的 HDS 活性高于 Ni_2P/Al_2O_3，例如在 260 ℃时，它们的 HDS 转化率分别为 66% 和 45%. Ni_2P 在 CS_2 硫化时物相没有发生变化，但有 1.1% 的 S 进入了催化剂，表明 Ni_2P 经 CS_2 硫化后有 Ni-P-S 表面物种生成，其 HDS 加氢活性高于纯 Ni_2P. NiS_x（P）/Al_2O_3 中也含有 3% 的 S，但其 HDS 活性却与 Ni_2P/Al_2O_3 差别不大，可能是由于 NiS_x（P）/Al_2O_3 中 Ni_2P 的粒径（13.0 nm）远大于 Ni_2P/Al_2O_3 的粒径（7.0 nm）. 可见，由于 S 的存在，NiS_x（P）/Al_2O_3 中 Ni_2P 的活性还是显著提高了. 因此，在 360 ℃，DBT 在这些催化剂上的转化率顺序为：Ni_2P（S）/Al_2O_3 > NiS_x（P）/Al_2O_3 > Ni_2P/Al_2O_3 >> NiS_x/Al_2O_3.

在产物选择性方面，随着反应温度提高，所有催化剂上生成环己基苯（CHB）的选择性增大，表明在这些催化剂上，DBT 的 HDS 反应以先加氢再脱硫路线为主，而非生成联苯（BP）产物的直接脱硫路线. 4 个催化剂上 HDS 反应生成 CHB 的选择性顺序为 Ni_2P/Al_2O_3 > NiS_x（P）/Al_2O_3 > Ni_2P（S）/Al_2O_3 > NiS_x/Al_2O_3，表明催化剂中的 S 不利于加氢脱硫反应路线.

在 260~360 ℃下，4 种催化剂都表现出很高的加氢脱氮活性，喹啉转化率均达到 100%. 虽然各催化剂上丙基环己烷（PCH）的选择性都随反应温度提高而提高，但不同催化剂对 PCH 的选择性也存在差异（较低温度下尤为明显）. 260 ℃时，NiS_x/Al_2O_3、Ni_2P/Al_2O_3、Ni_2P（S）/Al_2O_3 和 NiS_x（P）/Al_2O_3 上的 PCH 选择性依次为 30%、90%、80% 和 88%. 可见，Ni_2P 对喹啉的苯环加氢活性远高于硫化镍.

不同方法得到的磷化镍对四氢萘加氢精制反应的催化活性均远高于硫化镍. 例如，360 ℃时四氢萘在 NiS_x/Al_2O_3 上的转化率仅有 0.6%，但在 NiS_x（P）/Al_2O_3、Ni_2P/Al_2O_3 和 Ni_2P（S）/Al_2O_3 上四氢萘的转化率分别达到了 5.7%、9.2% 和 13.8%，与催化剂的 DBT 加氢脱硫活性顺序一致. 四氢萘在加氢精制反应中既可发生加氢反应生成反式和顺式十氢萘，也可发生脱氢反应生成萘. Ni_2P 的十氢萘选择性远高于 NiS_x，而含硫 Ni_2P 催化剂的十氢萘选择性则降低了，再次表明 Ni_2P 中含硫不利于芳环加氢反应.

1 Introduction

Nickel sulfides have various applications in the fields such as semiconductors, optoelectronics, energy and catalysis[1-5]. However, they are not highly active for the hydrotreating reactions[6-10], and were mainly used as promoters for the supported Ni-Mo-S and Ni-W-S catalysts[11-13]. On the other hand, the transition metal phosphides (especially Ni_2P) were found to be highly active for the hydrotreating reactions and expected to become a new generation of catalysts to play the same functions as the traditional catalysts of metal sulfides. In fact, different techniques have been developed for the preparation of metal phosphides, for example, the technique of temperature-programmed reduction (TPR), the gas phase phosphidation with PH_3 and liquid phase phosphidation with PPh_3[14-16].

Only a few comparative studies on the nickel sulfides and phosphides were reported in literature. Phimsen *et al.*[17] prepared a 15%Ni/Al_2O_3 catalyst, which was sulfided by H_2S/H_2 to nickel sulfides (Ni_3S_2 and Ni_3S_4) or phosphided by the TPR method to nickel phosphides ($Ni_{12}P_5$ and Ni_3P). They found that the nickel phosphides showed the higher hydrogenation and hydrodeoxygenation activities than the nickel sulfides while the nickel sulfides exhibited the lower methanation and cracking activities than the nickel phosphides for the production of bio-fuels from the spent coffee oil. Stinner *et al.*[18] found that the presence of H_2S in feed strongly inhibited the hydrodenitridation (HDN) activity of a Ni_2P catalyst, and the activity could not be recovered even after the removal of H_2S from the feed. The authors argued that Ni_2P was more stable than NiS_x and Ni_2P could not be sulfided by

H_2S so that the decrease of HDN activity must be due to the irreversible block of active sites of Ni_2P by the strongly adsorbed H_2S. However, others reported that sulfur could be incorporated into the surface of metal phosphides during the HDS reactions. For example, Oyama *et al.*[19-20] detected Ni-S bonds on the surface of used nickel phosphides, suggesting the formation of nickel phosphosulfide surface species, which might be the real active species for the HDS reactions. Wang *et al.*[21] found that the Ni_2P/MCM-41 passivated by H_2S was more active than that passivated by O_2 for the HDS reaction, and the catalyst with the higher HDS activity contained more sulfur after the reaction. The authors also suggested that the surface sulfides or phosphosulfide species were the active sites for the HDS reaction. Similar results were obtained on the FeP/SiO_2 prepared with FeS as the precursor[22]. Nelson *et al.*[23] indicated that up to 50% of surface P atoms in Ni_2P could be replaced by S according to their DFT calculations.

It is not easy to adequately compare nickel sulfides with phosphides since different precursors and preparation methods could significantly affect the composition and performance of catalysts. To a large extent, the relatively low HDS activities of nickel sulfides might be due to their low surface area, poor dispersion and thus little active sites[7-9]. It can be expected that more active sites and consequently higher HDS activity could be achieved with nickel sulfides. Recently, highly dispersed Ni_2P[16,24-27] and FexP[28-29] catalysts were prepared in our group, with the highly loaded (60%~80% weight percent) and dispersed precursors. The Ni_2P catalysts thus prepared possessed small particles and abundant active sites and exhibited high activities for the HDS reactions of dibenzothiophene (DBT). In particular, the phosphidation of the 80% Ni/Al_2O_3 (with the high H_2 uptake of 1017 μmol/g) generated a Ni_2P/Al_2O_3 catalyst with the CO uptake of 345 μmol/g, which is the highest value reported so far[26]. In this work, the similar nickel precursor was used to prepare nickel sulfides and compared with Ni_2P. However, since the nickel sulfides were prepared by the direct sulfidation with CS_2, Ni_2P in comparison must be prepared via the direct phosphidation with the same calcined precursor without the pre-reduction. In brief, the highly dispersed 80% Ni/Al_2O_3 catalyst was prepared, calcined and then sulfided by CS_2 or phophided by PPh_3 in liquid phases to obtain the highly dispersed nickel sulfides (NiS_x) or Ni_2P catalysts. Then the NiS_x (or Ni_2P) was further treated by PPh_3 (or CS_2) to observe the phase changes. All the catalysts were tested for the HDS of DBT, HDN of quinoline and hydrogenation of tetralin.

2 Experimental

2.1 Preparation of catalysts

The Ni/Al_2O_3 with about 80% Ni in weight was prepared by the co-precipitation method and dried with n-butanol[26]. In brief, desired amounts of Ni $(NO_3)_2$ and Al $(NO_3)_3$ were dissolved in 100 mL de-ionized water to obtain a solution, while desired amount of Na_2CO_3 was dissolved in 100 mL de-ionized water to obtain another solution. The two solutions were simultaneously added drop-wise into 200 mL de-ionized water under stirring at 80 ℃. The precipitate formed was washed thoroughly with de-ionized water, and then dispersed into 200 mL n-butanol which was evaporated at 80 ℃. The sample was then further dried at 120 ℃ for 12 h, and calcined in air at 350 ℃ for 3 h. The sample thus obtained was denoted as NiO/Al_2O_3.

The sample was sulfided by CS_2 in liquid phase[29-30]. Typically, the NiO/Al_2O_3 was loaded into a fix-bed reactor with an inner diameter of 10 mm and sandwiched with quartz sands. Then, a heptanes solution containing 2% (weight percentage) CS_2 was pumped into the reactor along with H_2 flow at a weight hourly space velocity (WHSV) of 2 h^{-1} and H_2/oil of 300 v/v. The reactor was heated from room temperature to 230 ℃ with a rate of 1 ℃/min, kept at 230 ℃ for 2 h, then heated to 310 ℃ with the same rate, and kept at 310 ℃ for 4 h. The sample thus sulfided directly was denoted as NiS_x/Al_2O_3.

The NiO/Al_2O_3 was phosphided by PPh_3 in liquid phase[26]. The procedure was similar to that of sulfidation above, but a heptane solution containing 2% (weight percentage) PPh_3 was used here. The

temperature was elevated to 320 ℃ with the rate of 1 ℃/min and kept at 320 ℃ for 36 h. The catalyst thus phosphided directly was denoted as Ni_2P/Al_2O_3.

Then, the NiS_x/Al_2O_3 was treated by PPh_3 with the same phosphidation procedure described above and the sample obtained was denoted as NiS_x (P)$/Al_2O_3$. Similarly, the Ni_2P/Al_2O_3 was treated by CS_2 with the same sulfidation procedure described above and the sample obtained was denoted as Ni_2P (S)$/Al_2O_3$.

2.2 Characterization of catalysts

The catalysts for characterizations were passivated before unloaded from the fix-bed reactor. X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6000 powder diffractometer using a Cu $K\alpha$ radiation (λ =0.1541 nm) at 40 kV and 30 mA. The 2θ scans covered the range of 10° to 80° with a speed of 6 (°)/min and a step of 0.02°. The chemical compositions of catalysts were analyzed by an ARL-9800 X-ray fluorescence spectrometer (XRF).

2.3 Catalytic tests

Model diesel containing 1.72% DBT, 0.185% quinoline, 5% tetralin and 0.5% n-octane (as an internal standard) in balanced n-tetradecane (solvent) was pumped into a tubular stainless steel fix-bed reactor with an inner diameter of 10 mm for the evaluation of catalysts at 260~360 ℃, 3.1 MPa with a WHSV of 2 h^{-1} and H_2/oil ratio of 1500 (v/v). The products were collected after 24 h when the activity was stabilized, and analyzed on a gas chromatograph equipped with a flame ionization detector (FID), a flame photometric detector (FPD) and a nitrogen-phosphorus detector (NPD).

3 Results and discussion

3.1 Phosphidation of NiS_x

Fig.1 shows the XRD patterns for the NiO/Al_2O_3, NiS_x/Al_2O_3 and the samples derived from the phosphidations of NiS_x/Al_2O_3 at 170~320 ℃ for 36 h, respectively. Only broad diffraction peaks for NiO (PDF 65-2901) were detected for the calcined sample (Fig.1 (a)), indicating that small NiO particles (about 3 nm) were highly dispersed on the support. When the NiO/Al_2O_3 was sulfided by CS_2 at 310 ℃, the diffraction peaks for NiO disappeared, and new peaks for Ni_3S_2 (PDF 44-1418) appeared at 2θ =21.7°, 31.1°, 37.7°, 44.3°, 49.7° and 55.2° and those for Ni_3S_4 (PDF 43-1469) appeared at 2θ =26.5°, 31.3°, 37.9°, 49.9° and 54.8° (Fig.1 (b)), indicating the formation of nickel sulfides (denoted as NiS_x) upon the direct sulfidation of NiO/Al_2O_3 by CS_2.

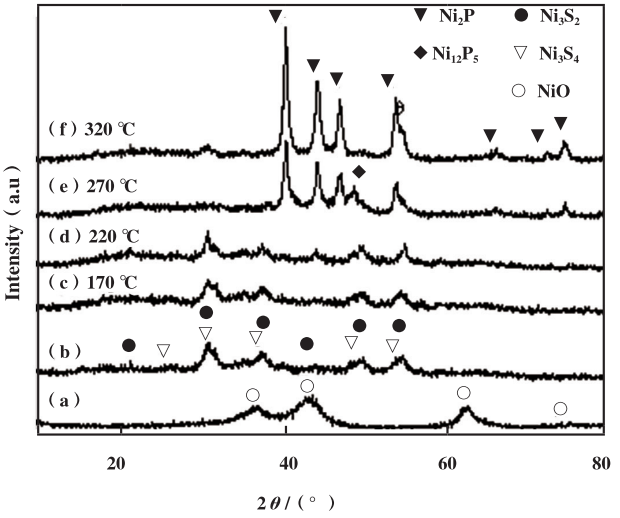

Fig.1 XRD patterns for the Ni/Al_2O_3 calcined at 350 ℃ (a), followed by sulfidation of (a) at 310 ℃ for 4 h (b) and then phosphidation of (b) at 170~320 ℃ for 36 h (c–f), respectively

Fig.1 (c–f) show the XRD patterns for the NiS_x/Al_2O_3 phosphided at different temperatures (170~320 ℃) for 36 h. When the NiS_x/Al_2O_3 was phosphided at 170 and 220 ℃, only Ni_3S_2 and Ni_3S_4 phases were observed (Fig.1 (c) and (d)), indicating that NiS_x could not be phosphided at the low temperatures. However, the intensities of diffraction peaks for NiS_x increased, indicating the increase in the crystalline sizes of NiS_x during the phosphidation. When the NiS_x/Al_2O_3 was phosphided at 270 ℃, the diffraction peaks for NiS_x disappeared, and the diffraction peaks for Ni_2P (PDF 65-1989) appeared at 2θ =40.7°, 44.6°, 47.4° and 54.2° and those for $Ni_{12}P_5$ (PDF 22-1190) appeared at 2θ =48.9° (Fig.1 (e)), indicating the replacement of S in NiS_x by P during the process. When the phosphidation temperature increased to 320 ℃, the diffraction peak for $Ni_{12}P_5$ disappeared while the intensities of peaks for Ni_2P increased significantly (Fig.1 (f)),

indicating the complete conversion of NiS_x to Ni_2P (NiS_x (P)/Al_2O_3) and growing of the Ni_2P particles.

Table 1 summarizes the information of the phases and crystalline sizes for the samples (a–f) in Fig.1. The crystalline size of NiO obtained by the calcination of Ni/Al_2O_3 at 350 ℃ was estimated to be about 3 nm, while the direct sulfidation led to the formation of NiS_x with the average crystalline size of about 5.8 nm. Although the NiS_x was not phosphided by PPh_3 at the lower temperatures, the crystalline sizes of NiS_x were gradually increased to 8.4 nm. When NiS_x was phosphided at 320 ℃ , the crystalline size of formed Ni_2P grew larger to about 13.3 nm.

Table 1 Phases and crystalline sizes in the catalysts prepared by different methods

Samples in Fig.1	XRD phase	D /nm
a	NiO	3.0
b	Ni_3S_2, Ni_3S_4	5.8
c	Ni_3S_2, Ni_3S_4	5.8
d	Ni_3S_2, Ni_3S_4	8.4
e	Ni_2P/$Ni_{12}P_5$	11.7/8.2
f	Ni_2P	13.3

Notes: The crystalline sizes (D) were estimated by the Scherrer equation according to the full width at half maximum (FWHM) of the peaks at 43.2° (NiO), 40.8° (Ni_2P), 48.9° ($Ni_{12}P_5$) and 31.1° (Ni_3S_2), respectively, in the XRD patterns.

3.2 Sulfidation of Ni_2P

Fig.2 shows the XRD patterns for the NiO/Al_2O_3, Ni_2P/Al_2O_3 and those obtained by the sulfidation of Ni_2P/Al_2O_3 at 310~360 ℃ , respectively. When the NiO/Al_2O_3 was phosphided by PPh_3 at 320 ℃ , pure Ni_2P phase was obtained (Fig.2 (b)). However, when the Ni_2P/Al_2O_3 was treated by CS_2 at even higher temperature (360 ℃), the Ni_2P was still the only phase detected by XRD, indicating that the Ni_2P was significantly more stable than the sulfide phases (Ni_3S_2 and Ni_3S_4), and highly resistant to S poisoning.

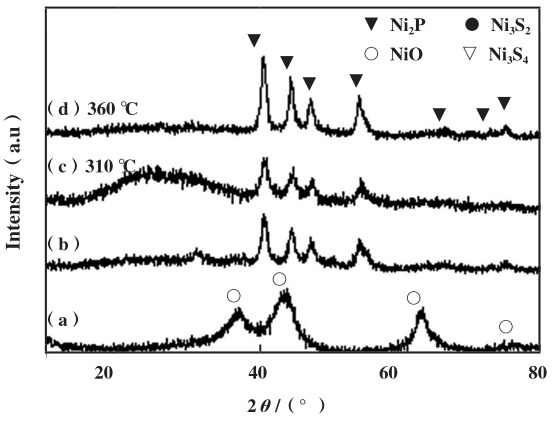

Fig.2 XRD patterns for the Ni/Al_2O_3 calcined at 350 ℃ (a), followed by phosphidation of (a) at 320 ℃ for 36 h (b) and then sulfidation of (b) at 310~360 ℃ for 4 h (c and d), respectively

Table 2 displays the changes in the phases and crystalline sizes for the samples shown in Fig.2. The crystalline size of Ni_2P obtained by the direct phosphidation of NiO/Al_2O_3 with PPh_3 was about 7.0 nm. When the Ni_2P/Al_2O_3 was treated by CS_2 at 310 ℃ , both the Ni_2P phase and the crystalline size (6.7 nm) did not change. When it was treated at 360 ℃ , the Ni_2P phase still remained, but the crystalline size of Ni_2P increased to 9.5 nm, which was still significantly smaller than that formed by the phosphidation of NiS_x at 320 ℃ (13.3 nm), indicating the high stability of phase and crystalline size of Ni_2P.

Table 2 Phases and crystalline sizes in the catalysts prepared by different procedures

Samples in Fig.2	XRD phase	D /nm
a	NiO	3.0
b	Ni_2P	7.0
c	Ni_2P	6.7
d	Ni_2P	9.5

Notes: The crystalline sizes (D) were estimated by the Scherrer equation according to the full width at half maximum (FWHM) of the peaks at 43.2° (NiO) and 40.8° (Ni_2P) respectively, in the XRD patterns.

Table 3 summarizes the information about the phases, crystalline sizes and compositions for the NiS_x/Al_2O_3, Ni_2P/Al_2O_3, NiS_x (P)/Al_2O_3 (NiS_x/Al_2O_3 phosphided at 320 ℃) and Ni_2P (S)/Al_2O_3 (Ni_2P/Al_2O_3

sulfided at 310 ℃). It is seen that only 3% sulfur remained in the NiS_x (P)/Al_2O_3, i. e., most S in the NiS_x was replaced by P upon the phosphidation of NiS_x at 320 ℃ . In contrast, only 1.1% sulfur was incorporated into the Ni_2P (S)/Al_2O_3 when the Ni_2P/Al_2O_3 was treated by CS_2 at 310 ℃ , indicating that Ni_2P was highly resistant to sulfur. The P/Ni atom ratios in the NiS_x (P)/Al_2O_3 and Ni_2P (S)/Al_2O_3 were similar (0.74), higher than the stoichiometric ratio of 0.5 for Ni_2P, probably due to the presence of some other phosphorus species in the catalysts [16].

Table 3 Phases and crystalline sizes as well as chemical compositions analyzed by XRD and XRF for the catalysts prepared by different procedures

Catalyst	XRD Phase	D /nm	Ni/%	P/%	S/%	P/Ni (atom)	S/Ni (atom)
NiS_x/Al_2O_3	Ni_3S_2, Ni_3S_4	5.8	–	–	–	–	–
Ni_2P/Al_2O_3	Ni_2P	7.0	–	–	–	–	–
NiS_x(P)/Al_2O_3	Ni_2P	13.3	49.3	19.4	3.0	0.74	0.11
Ni_2P(S)/Al_2O_3	Ni_2P	6.7	51.6	20.3	1.1	0.74	0.04

3.3 Hydrotreating activities of nickel sulfides and phosphides

The catalysts NiS_x/Al_2O_3, Ni_2P/Al_2O_3, NiS_x (P)/Al_2O_3 and Ni_2P (S)/Al_2O_3 were compared for the hydrotreating reactions. Fig.3 shows the XRD patterns of the used catalysts after the hydrotreating reactions. It is seen that NiS_x and Ni_2P phases in NiS_x/Al_2O_3 (7.7 nm) and Ni_2P/Al_2O_3 (8.0 nm) remained after the reactions (Fig.3 (a) and (c)), indicating that both NiS_x and Ni_2P phases were stable during the HDS reactions.

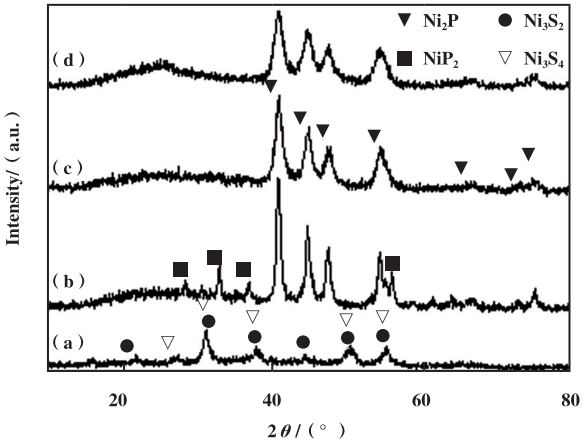

Fig.3 XRD patterns for the used catalysts after the HDS reactions: NiS_x/Al_2O_3 (a), NiS_x(P)/Al_2O_3 (b), Ni_2P/Al_2O_3 (c) and Ni_2P(S)/Al_2O_3 (d)

The diffraction peaks for Ni_2P in the NiS_x(P)/Al_2O_3 also remained with similar intensities (~13.0 nm) after the HDS reactions (Fig.3 (b)). However, some diffraction peaks for NiP_2 (PDF 21-0590) were observed in the used catalyst after the HDS reaction. The reaction of Ni_2P with extra P in the catalyst during the HDS reaction might account for the formation of NiP_2.

The diffraction peaks for Ni_2P in the Ni_2P(S)/Al_2O_3 did not seem to change (7.0 nm) after the HDS reactions (Fig.3 (d)), indicating the high stability of Ni_2P in this catalyst.

Fig.4 (a) shows the activities of the NiS_x(P)/Al_2O_3, Ni_2P/Al_2O_3, NiS_x (P)/Al_2O_3 and Ni_2P (S)/Al_2O_3 for the HDS of DBT. Apparently, the Ni_2P/Al_2O_3 catalysts were significantly more active than the NiS_x/Al_2O_3. It is known that the Ni_2P was more active than sulfide catalysts for the hydrotreating reactions [14]. However, the comparisons were usually made between Ni_2P and the commercial Ni-Mo-S catalysts [14,20,31-33]. In the current work, the Ni_2P and NiS_x were prepared from the same precursor. In addition, the NiS_x/Al_2O_3 (without Mo) prepared in this work showed the high activity for the HDS reaction. The conversion of DBT reached 75% at 360 ℃ . This must due to that the NiS_x/Al_2O_3 catalysts were prepared from the highly dispersed NiO/Al_2O_3 with small NiO particles (~ 3 nm).

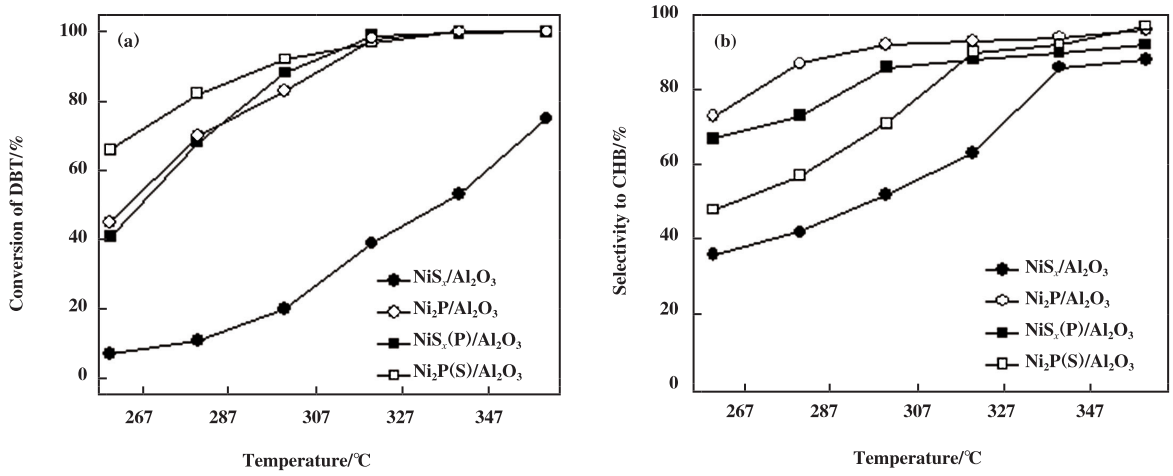

Fig.4 Conversion of DBT (a) and selectivity to cyclohexylbenzene (CHB) (b) over the catalysts

Reaction conditions: P=3.1 MPa, WHSV=2 h^{-1} and H_2/oil=1500 (v/v)

It is worth noting that the Ni_2P (S)/Al_2O_3 was more active than the Ni_2P/Al_2O_3 for the HDS of DBT. For example, at 260 ℃, the conversion of DBT over the Ni_2P (S)/Al_2O_3 and Ni_2P/Al_2O_3 was about 66% and 45%, respectively. Some authors [19-22,34] proposed that the M-P-S (M=metal) species formed on the surfaces of transition metal phosphides during the HDS reactions might be the real active species. When the Ni_2P/Al_2O_3 was treated with CS_2, the phase of Ni_2P did not change, but some S (1.1%) was incorporated into the Ni_2P (S)/Al_2O_3 according to the XRF analysis. Thus, our current result agreed well with reported that surface Ni-P-S species must be more active than pure Ni_2P for the HDS reactions.

The NiS_x (P)/Al_2O_3 contained 3% sulfur exhibited the similar activity to the Ni_2P/Al_2O_3 for the HDS reaction. However, the crystalline size of Ni_2P in the NiS_x (P)/Al_2O_3 was significantly larger (13.3 nm) than that in the Ni_2P/Al_2O_3 (7.0 nm). Thus, the HDS activity of Ni_2P in the NiS_x (P)/Al_2O_3 was significantly higher than that in the Ni_2P/Al_2O_3, due to the presence of S.

The above results showed that the conversion of DBT at 360 ℃ followed the order of Ni_2P (S)/Al_2O_3 > NiS_x (P)/Al_2O_3 ~ Ni_2P/Al_2O_3 >> NiS_x/Al_2O_3.

Fig.4 (b) shows the selectivities for the HDS of DBT over the catalysts at different temperatures. With the increase of temperature, the selectivity to cyclohexylbenzene (CHB) increased over all the four catalysts. The high selectivity to CHB indicated that the HDS of DBT underwent mainly through the indirect desulfurization route (HYD) over the catalysts, where the desulfurization occurred after an aromatic ring in DBT was hydrogenated, rather than the direct desulfurization route (DDS) with the formation of biphenyl. It is also seen that the selectivity to CHB over the catalysts followed the order of Ni_2P/Al_2O_3 > NiS_x (P)/Al_2O_3 > Ni_2P (S)/Al_2O_3 > NiS_x/Al_2O_3, indicating that the presence of sulfur might be unfavorable to the HYD route over Ni_2P for the HDS of DBT.

Fig.5 shows the results for the conversion of quinoline and selectivity to propyl-cyclohexane (PCH) over the catalysts at different temperatures. The conversion of quinoline over all the catalysts reached 100% at 260~360 ℃, indicating the high HDN activity of these catalysts. Although the selectivity to PCH increased with temperature over the catalysts, the catalysts exhibited different selectivities to PCH (especially at low temperatures). For example, the selectivity to PCH at 260 ℃ over the NiS_x/Al_2O_3, Ni_2P/Al_2O_3, Ni_2P (S)/Al_2O_3 and NiS_x (P)/Al_2O_3 were about 30%, 90%, 80% and 88%, respectively, indicating that Ni_2P was much more active than NiS_x for the hydrogenation of aromatic ring in quinoline.

Fig.6 (a) shows the conversions of tetralin over the catalysts. It is seen again that the Ni_2P (S)/Al_2O_3 catalyst exhibited much higher activities than the

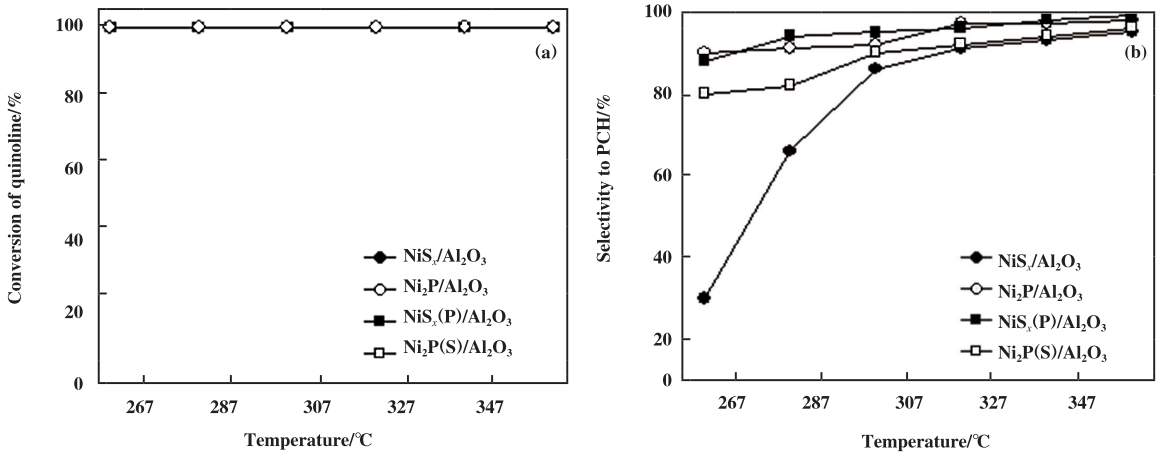

Fig.5 Conversion of quinoline (a) and selectivity to propyl-cyclohexane (PCH) (b) over the catalysts

Reaction conditions: P=3.1 MPa, WHSV=2 h^{-1} and H_2/oil=1500 (v/v)

Ni_2P/Al_2O_3 and NiS_x/Al_2O_3 catalysts. For example, the conversion of tetralin at 360 ℃ was only 0.6% over the NiS_x/Al_2O_3, while that was 5.7%, 9.2% and 13.8% over the $NiS_x(P)/Al_2O_3$, Ni_2P/Al_2O_3 and $Ni_2P(S)/Al_2O_3$, respectively, in consistence with the results for the HDS of DBT.

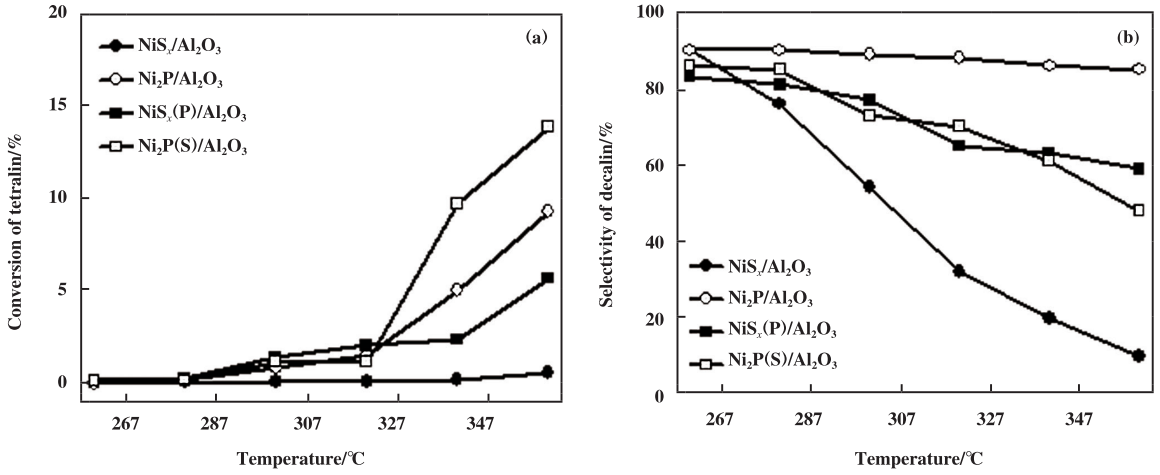

Fig.6 Conversion of tetralin (a) and the selectivity to decalin (b) over the catalysts

Reaction conditions: P=3.1 MPa, WHSV=2 h^{-1} and H_2/oil=1500 (v/v)

Tetralin might be hydrogenated to decalin or dehydrogenated to naphthalene during the hydrotreating reactions. Fig.6 (b) shows the selectivity to decalin over the catalysts. Apparently, Ni_2P exhibited much higher selectivity to decalin than NiS_x, and the Ni_2P catalysts containing a small amount of S showed the moderate selectivities, indicating again that the presence of S was unfavorable to the hydrogenation of aromatic rings.

4 Conclusions

A highly loaded and dispersed 80% Ni/Al_2O_3 catalyst was prepared and calcined at 350 ℃ to obtain a NiO/Al_2O_3 sample with small NiO particles (~ 3 nm). Then the NiO/Al_2O_3 was sulfided by CS_2 at 310 ℃ to NiS_x/Al_2O_3 (Ni_3S_2 and Ni_3S_4) or phosphided by PPh_3 at 320 ℃ to Ni_2P/Al_2O_3.

When the NiS_x/Al_2O_3 was phosphided with PPh_3 at 320 ℃ , NiS_x was converted into Ni_2P (13.3 nm) (NiS_x (P) $/Al_2O_3$), which was as active as the directly phosphided Ni_2P/Al_2O_3 (7.0 nm), indicating that the Ni-P-S species must be more active than the Ni-P species for the HDS of DBT, consistent with the results

reported [20–21].

When the Ni_2P/Al_2O_3 was treated with CS_2 at 310~360 ℃, the Ni_2P phase did not change, indicating that Ni_2P was much more stable than NiS_x (Ni_3S_2 and Ni_3S_4). Moreover, the Ni_2P (S)$/Al_2O_3$ (6.7 nm) treated with CS_2 at 310 ℃ was more active than the directly phosphided Ni_2P/Al_2O_3 (7.0 nm), indicating again that the Ni-P-S species must be more active than the Ni-P species for the HDS of DBT.

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Stability and Activity of Ni_2P and NiS_x for the Hydrotreating Reactions

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Abstract: A highly dispersed 80% Ni/Al_2O_3 catalyst was prepared by the co-precipitation method, which was calcined in air at 350 ℃ to obtain a highly dispersed NiO/Al_2O_3 with NiO particles of about 3 nm. The NiO/Al_2O_3 was then sulfided with CS_2 at 310 ℃ to nickel sulfides (Ni_3S_2 and Ni_3S_4 of about 5.8 nm) , or phosphided with PPh_3 at 320 ℃ to Ni_2P (7.0 nm) . The NiS_x phases were completely converted into Ni_2P (13.3 nm) when phosphided with PPh_3 at 320 ℃ , which was as active as the directly phosphided Ni_2P (7.0 nm) . In contrast, the phase and crystalline size of Ni_2P did not change when treated with CS_2 even at 360 ℃ , indicating that the Ni_2P was much more stable than the NiS_x (Ni_3S_2 and Ni_3S_4) . Moreover, the Ni_2P/Al_2O_3 treated with CS_2 at 310 ℃ was more active than the directly phosphided Ni_2P for the hydrodesulfication (HDS) reaction, indicating that the incorporation of S into Ni_2P might generate some Ni-P-S species that were more active than the Ni-P surface species for the HDS reactions.

Key words: Ni_2P/Al_2O_3 catalyst; NiS_x/Al_2O_3 catalyst; liquid phase phosphidation by PPh_3; liquid phase sulfidation by CS_2; phase stability; hydrotreating reaction