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Effects of calcination and reduction temperature on the properties of Ni-P/SiO₂ and Ni-P/Al₂O₃ and their hydrodenitrogenation performance†

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A series of SiO₂-supported and γ -Al₂O₃-supported nickel phosphides were prepared by temperature-programmed reduction (TPR) with different calcination and reduction temperatures. The prepared catalysts were characterized by XRD, BET, H₂-TPR, CO titration and HRTEM. The crystal phase and CO uptake content were influenced by calcination and reduction temperature. The catalytic performance of various catalysts was tested in quinoline hydrodenitrogenation and exhibited considerable differences. The quinoline HDN activity of SiO₂-supported nickel phosphides decreases with increase of calcination and reduction temperature. In contrast to SiO₂-supported samples, the ability to remove nitrogen of γ -Al₂O₃-supported samples increases with reduction temperature.

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Introduction

Nickel phosphides as novel hydrotreating catalysts have received much attention.^{1–3} They are widely investigated in hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO), and exhibit special catalytic activity. The excellent catalytic activity is attributed to the ensemble and ligand effects.^{4,5} In comparison with conventional sulfided catalysts, nickel phosphide catalysts show higher HDS and HDN activity.^{6,7} For example, Sawhill *et al.* observed that Ni₂P/SiO₂ catalysts were approximately 15 and 3.5 times more active than conventional sulfided Mo/SiO₂ and Ni-Mo/SiO₂ catalysts in thiophene HDS.⁸ SiO₂ and Al₂O₃ are widely used as supports in a variety of studies. Nevertheless, nickel phosphide catalysts supported on SiO₂ and Al₂O₃ exhibit very different catalytic activity in HDN and HDS.⁹ Moreover, when Al₂O₃ is used as a support, more phosphide is used to produce Ni₂P because phosphide reacts with aluminum to form AlPO₄.

Some researchers obtained highly active nickel phosphide catalysts with different method at low pretreatment temperature. For example, PH₃ was used to form Ni₂P and the particle size of Ni₂P is similar to initial NiO.¹⁰ Though nickel phosphide catalysts with various preparation methods are obtained, the most widely used method is temperature-programmed

reduction (TPR).¹¹ The method of TPR includes dry, calcination, reduction and passivation. In fact, every step above exerts a certain extent of influence on the catalytic activity. Wang *et al.* observed that Ni₂P/SiO₂ suffered from calcination exhibited lower HDN activity than uncalcined catalysts.¹² They attributed the low HDN activity to the less amount of Ni⁰ caused by calcination, leading to low hydrogenation ability. Alexander and Kevin found that the passivated Ni₂P/SiO₂ possesses less CO uptake content after secondary reduction.¹³ It is suggested that the catalyst suffered from sintering or reconstruction during the secondary reduction.

The commonly characterized means include XRD, H₂-TPR, TEM, CO titration and so on. H₂-TPR was a common and important characterization means, which could provide the information about the species types and reducibility of nickel phosphides. Generally, most researchers perform H₂-TPR experiments with heating rate of 10 °C min^{−1} or so to study the basic property of nickel phosphide catalysts.^{14,15} However, the heating rate during catalytic test is usually 1 °C min^{−1} or so. Furthermore, the different heating rate may provide different reduction curves.¹¹ Consequently, the heating rate during characterization in line with test condition may provide more accurate and useful information. Up to now, heating rate of 1 °C min^{−1} is few reported during H₂-TPR characterization of nickel phosphides. In our study, heating rate of 1 °C min^{−1}, 3 °C min^{−1}, 10 °C min^{−1} were all investigated. Previously, Rodriguez *et al.* performed time resolved XRD experiments for Ni₂P/SiO₂ and explicitly explained the transformation way of Ni₂P precursors at ramp rate of 15 °C min^{−1}.¹⁶ However, the influence of specific reduction temperature on the catalytic activity has not been investigated. The phenomenon observed at high heating rate of 15 °C min^{−1} is also a great difference from fact experimental condition at 1 °C min^{−1}.

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Experimental

Catalyst preparation

Precursors of 30 wt% nickel phosphide supported on SiO₂ were prepared with Ni and P atomic ratio of 1.25. This atomic ratio was proved to be optimal for quinoline HDN under the currently experimental conditions. Specifically, 3 g NH₄H₂PO₄ and 9.2 g Ni(NO₃)₂·6H₂O was added into 100 mL deionized water and then adjusted the pH to 2–3 by HNO₃. Subsequently, 10 g SiO₂ was poured into the above solution, stirring at 80 °C for 4 h. The samples were dried at 120 °C overnight and calcined at 440, 500, 560, 620 °C respectively for 5 h. TPR method was used to reduce the precursors. Each precursor was heated from room temperature to 560, 650 or 750 °C at a rate of 1 °C min^{−1} with a 50 mL min^{−1} H₂. Nickel phosphide catalysts were passivated with 0.5 vol% O₂/N₂ at room temperature for 6 h. The resulting catalysts were denoted as Ni-P_x^y/SiO₂, where *x* represents calcination temperature and *y* represents reduction temperature.

Samples of 30 wt% nickel phosphide supported on Al₂O₃ were prepared with Ni and P atomic ratio of 1.4. The synthesized steps were similar to Ni-P_x^y/SiO₂. And the obtained catalysts were also denoted as Ni-P_x^y/Al₂O₃.

Characterization method

A Rigaku D/max-2500 apparatus was used to carry out XRD experiments with a step of 4° s^{−1} over the 2θ range of 10–80°. The specific surface area was obtained on a Tristar-3020 and calculated on the basis of the BET isothermal equation. H₂ temperature programmed reduction (H₂-TPR) was performed using a Quantachrome ChemBET Pulsar TPR/TPD instrument equipped with a thermal conductivity detector (TCD). A sample (≈0.03 g) was firstly dried at 400 °C for 2 h in flowing He (50 mL min^{−1}). Subsequently, the sample was cooled to 80 °C and the He was changed into H₂/Ar. Finally, when the TCD signal reached stable reduction was conducted at a heating rate of 1, 3 and 10 °C min^{−1} in H₂/Ar (75 mL min^{−1}). The hydrogen consumption was determined by a TCD. Before detection, the gas was passed through a cold trap. A cold trap filled with a mixture of liquid nitrogen and acetone was employed to remove the produced water. Carbon monoxide (CO) uptakes over the samples were by a pulse injection method on a Quantachrome ChemBET Pulsar TPR/TPD instrument to estimate the content of active sites on the catalysts. Prior to injection of CO, the samples (0.25 g, 20–40 mesh) was firstly reduced in H₂/Ar (60 mL min^{−1}) at 450 °C for 2 h and then cooled to 30 °C in He (60 mL min^{−1}). Pulses of CO (50 μL, 10% CO/He) were injected in a He carrier until stable of the peak. A JEOL JEM-2100 F apparatus was used to obtain the transmission electron microscopy (HRTEM) image. The reduction samples were placed in ethanol with an ultrasonic dispersion for 1 hour and deposited on a Cu grid, and then the samples were dried at room temperature overnight. Determination of Ni and P contents was carried out using an ICP method with JY/T 015-1996 apparatus. Lewis and Brønsted acid density were determined by pyridine adsorption infrared (Py-IR) means using a Thermo Nicolet-380 apparatus. The corresponding samples (≈15 mg) were pressed

into thin wafers and evacuated *in situ* under vacuum at 300 °C for 2 h (10^{−2} Pa) and then cooled to room temperature and collected the spectra of samples. After that, pyridine was dosed into the cell for 20 min. The sample was heated to 100 °C and kept for 30 min and then cooled to 40 °C and collected the spectra. Similarly, spectra treated at 200 °C was also obtained.

HDN catalytic test

Quinoline HDN test was performed. The quinoline HDN test of Ni-P/SiO₂ and Ni-P/γ-Al₂O₃ catalysts was conducted in a fixed-bed reactor with a mixture of 5000 ppm quinoline in decalin. 1 g passivated catalysts in 10–20 mesh size were loaded into the reaction tube. Prior to the catalytic test, the passivated catalysts were reduced in a 50 mL min^{−1} H₂ flow at 450 °C for 2 h. After that, the temperature was cooled to 360 °C. The quinoline solution was pumped into the fixed-bed reactor with a 3 g h^{−1} flow. The H₂/feed volumetric ratio was 1000 and H₂ pressure was 4 MPa.

The collected products after 12 h were qualitatively analyzed by an Agilent-5975C gas chromatograph-mass spectrometer and quantitatively analyzed by a Huaai 9560 gas chromatograph. To examine the stability of the Ni-P_x⁵⁶⁰/SiO₂ and Ni-P_x⁷⁵⁰/Al₂O₃ (*x* = 440, 500, 560, 620), the corresponding products were analyzed at time intervals of 24 h for a total time of 192 h.

The HDN conversion (HDN_C) of quinoline over the catalysts was expressed by the following equation:

$$\text{HDN}_C(\%) = \frac{n_{\text{PB}} + n_{\text{PCH}} + n_{\text{PCHE}}}{n_{\text{Q}} + \sum n_i}$$

where *n*_Q, *n*_{PCHE}, *n*_{OPA}, *n*_{PB}, and *n*_{PCH} represents the quinoline, propylcyclohexene, *ortho*-propylaniline, propylbenzene and propylcyclohexane concentration collected in the products, respectively. $\sum n_i$ represents the sum of all products concentration produced from quinoline, including 1,2,3,4-tetrahydroquinoline (THQ₁), 5,6,7,8-tetrahydroquinoline (THQ₅), decahydroquinoline (DHQ), *ortho*-propylaniline (OPA), propylbenzene (PB), propylcyclohexene (PCHE) and propylcyclohexane (PCH).

From the HDN conversion values, the turnover frequencies (TOFs) were calculated according to:

$$\text{TOF}(\text{h}^{-1}) = \frac{F_{\text{A0}}(\mu\text{mol h}^{-1}) \times \text{HDN}_C}{m(\text{g}) \times \text{chemisorption uptake}(\mu\text{mol g}^{-1})} \quad (1)$$

where *F*_{A0} is the molar flow of the quinoline feed (μmol h^{−1}).

Rate constants were calculated considering a first order kinetic by the following eqn (2):^{17,18}

$$k(\text{mol kg}^{-1} \text{h}^{-1}) = -\frac{F_{\text{A0}}}{M} \ln(1 - \text{HDN}_C) \quad (2)$$

where *k* is the rate constant (mol kg^{−1} h^{−1}), *F*_{A0} the molar flow of the quinoline feed (mol h^{−1}), *M* the weight of catalysts (kg), HDN_C the denitrogenation conversion of quinoline.

Results and discussion

XRD patterns of SiO₂-supported and γ-Al₂O₃-supported nickel phosphides are given in Fig. 1. For SiO₂-supported nickel



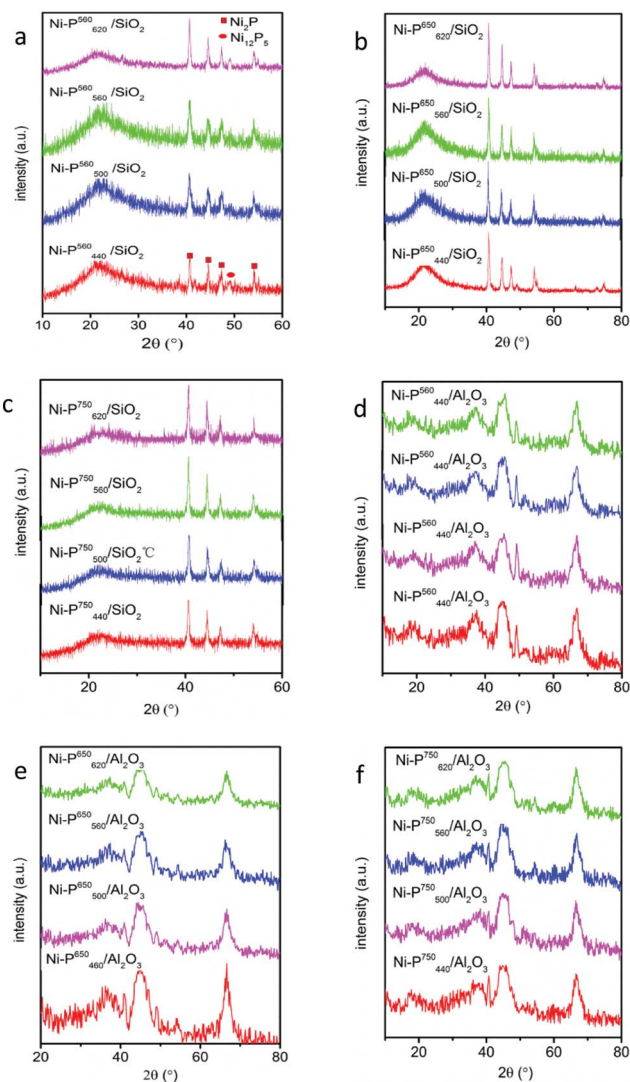


Fig. 1 XRD patterns of different SiO_2 -supported nickel phosphides reduced at (a) 560 °C, (b) 650 °C, (c) 750 °C and different $\gamma\text{-Al}_2\text{O}_3$ -supported nickel phosphides reduced at (d) 560 °C, (e) 650 °C, (f) 750 °C.

phosphides, the broad peak ($\approx 21^\circ$) is attributed to SiO_2 (PDF#27-0605). At reduction temperature of 560 °C, diffraction peaks assigned to Ni_{12}P_5 (PDF#22-1190) and Ni_2P (PDF#3-953) both appeared, and the main crystal phase is Ni_2P rather than Ni_{12}P_5 . With increasing reduction temperature to 650 and 750 °C, only diffraction peak of Ni_2P is observed. For $\text{Ni-P}/\gamma\text{-Al}_2\text{O}_3$, the broad peaks ($\approx 45^\circ$, 67°) are attributed to $\gamma\text{-Al}_2\text{O}_3$ (PDF#29-0063). It is shown that mere diffraction peak of Ni_{12}P_5 appeared at reduction temperature of 560 °C. But Ni_{12}P_5 and Ni_2P are observed at 650 and Ni_{12}P_5 diffraction peak became weak at 750 °C. It is also seen that the diffraction intensity of Ni_2P increased with calcination temperature at the same reduction temperature for $\text{Ni-P}/\text{SiO}_2$, indicating that the particle size increased with calcination temperature. XRD characterization of $\text{Ni-P}_{440}/\text{SiO}_2$ reduced at 460 and 520 °C was also performed and the result was presented in Figure S1.† It is observed that at reduction temperature of 460 °C, peak assigned

to Ni_{12}P_5 appeared. Up to 520 °C, peak attributed to Ni_2P was also detected. However, in the previous report, crystal phase of Ni_{12}P_5 appears at 550 °C and Ni_2P begins to form at 600 °C, while in our study the corresponding crystal was detected at lower temperature.⁸

The specific surface area (S_{BET}) of SiO_2 -supported and $\gamma\text{-Al}_2\text{O}_3$ -supported nickel phosphides was presented in Table 1 and their variation tendency of S_{BET} shows similar. The S_{BET} decreased as the reduction temperature increased for the samples with certain calcination temperature. For the sample with certain reduction temperature, the S_{BET} also decreased with increasing the calcination temperature. By increasing calcination and reduction temperature, crystal phase suffered from sintering and particle size became larger, leading to diminish of S_{BET} .

CO titration results are presented in Table 1. The CO uptake content declined as calcination temperature increased on account of growth of particle for both SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ -supported catalysts with determinate reduction temperature.

There are two aspects causing the decline of CO uptake content with increasing the reduction temperature. On one side, transformation of crystal phase occurred during reduction process. For example, both Ni_{12}P_5 and Ni_2P existed for $\text{Ni-P}^{560}/\text{SiO}_2$. While only Ni_2P was detected for $\text{Ni-P}^{650}/\text{SiO}_2$. On the other side, particle size tends to become larger.

H_2 -TPR patterns of SiO_2 -supported and $\gamma\text{-Al}_2\text{O}_3$ -supported nickel phosphides are presented in Fig. 2. H_2 -TPR patterns obtained at heating rate of $10^\circ\text{C min}^{-1}$ are shown in Fig. 2a and b. The two broad peaks at about 570 and 660 °C are assigned to reduction of nickel species and P–O bond for $\text{Ni-P}/\text{SiO}_2$. For

Table 1 Physical and chemical properties of different SiO_2 -supported nickel phosphides and $\gamma\text{-Al}_2\text{O}_3$ -supported nickel phosphides

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	CO uptake ($\mu\text{mol g}^{-1}$)
$\text{Ni-P}_{440}^{560}/\text{SiO}_2$	262	36
$\text{Ni-P}_{500}^{560}/\text{SiO}_2$	257	36
$\text{Ni-P}_{560}^{560}/\text{SiO}_2$	253	35
$\text{Ni-P}_{620}^{560}/\text{SiO}_2$	250	32
$\text{Ni-P}_{440}^{650}/\text{SiO}_2$	257	19
$\text{Ni-P}_{500}^{650}/\text{SiO}_2$	253	18
$\text{Ni-P}_{560}^{650}/\text{SiO}_2$	250	18
$\text{Ni-P}_{620}^{650}/\text{SiO}_2$	247	17
$\text{Ni-P}_{440}^{750}/\text{SiO}_2$	252	16
$\text{Ni-P}_{500}^{750}/\text{SiO}_2$	249	16
$\text{Ni-P}_{560}^{750}/\text{SiO}_2$	248	14
$\text{Ni-P}_{620}^{750}/\text{SiO}_2$	247	14
$\text{Ni-P}_{440}^{560}/\text{Al}_2\text{O}_3$	182	174
$\text{Ni-P}_{500}^{560}/\text{Al}_2\text{O}_3$	180	172
$\text{Ni-P}_{560}^{560}/\text{Al}_2\text{O}_3$	178	168
$\text{Ni-P}_{620}^{560}/\text{Al}_2\text{O}_3$	174	163
$\text{Ni-P}_{440}^{650}/\text{Al}_2\text{O}_3$	180	121
$\text{Ni-P}_{500}^{650}/\text{Al}_2\text{O}_3$	177	118
$\text{Ni-P}_{560}^{650}/\text{Al}_2\text{O}_3$	175	113
$\text{Ni-P}_{620}^{650}/\text{Al}_2\text{O}_3$	173	109
$\text{Ni-P}_{440}^{750}/\text{Al}_2\text{O}_3$	178	63
$\text{Ni-P}_{500}^{750}/\text{Al}_2\text{O}_3$	176	62
$\text{Ni-P}_{560}^{750}/\text{Al}_2\text{O}_3$	174	60
$\text{Ni-P}_{620}^{750}/\text{Al}_2\text{O}_3$	172	58



Ni-P/ γ -Al₂O₃, the peak becomes wider resulting from strong interaction between phosphide and γ -Al₂O₃. In the case of Ni-P₅₆₀/ γ -Al₂O₃ and Ni-P₆₂₀/ γ -Al₂O₃, reduction still occurs beyond 800 °C because of the existence of AlPO₄.¹⁹ However, no obvious reduction peak is seen for Ni-P₄₄₀/ γ -Al₂O₃ and Ni-P₅₀₀/ γ -Al₂O₃. Fig. 2c and d show the H₂-TPR patterns obtained at heating rate of 3 °C min⁻¹. It is seen that the peak shape is similar to the patterns obtained at heating rate of 10 °C min⁻¹. Nevertheless, the peaks of both SiO₂-supported and γ -Al₂O₃-supported nickel phosphides were shifted to lower temperature. In the case of Ni-P/SiO₂, reduction was completed at approximately 620 °C. Fig. 2e and f show the H₂-TPR patterns obtained at heating rate of 1 °C min⁻¹. It is seen that the peaks shifted to lower temperature. In addition, only single peak (\approx 500 °C) was observed for Ni-P/SiO₂. Reduction was almost finished at

560 °C. In addition, for the samples reduced at 10 °C min⁻¹ the amount of H₂ consumed was contrasted with the theoretical amounts of H₂ needed to form the phosphide phases in each catalyst. The calculated results were listed in Tables S1 and S2.[†] According to Tables S1 and S2,[†] the SiO₂ and Al₂O₃-supported catalysts both shown lower consumption than the theoretical value. Furthermore, for Al₂O₃-supported catalysts the molar ratio of true consumption of H₂ to theoretical consumption of H₂ was lower than the SiO₂-supported catalysts. For SiO₂-supported catalysts, P_xO_y could be produced, which was not able to be reduced. However, for Al₂O₃-supported catalysts a large amount of AlPO₄ was also produced but P_xO_y.⁸

Quinoline HDN catalytic test

Catalytic test with a variety of SiO₂-supported and γ -Al₂O₃-supported nickel phosphides was carried out and results are presented in Table 2. Apparently, it is seen that there are considerable HDN activity difference between SiO₂-supported and γ -Al₂O₃-supported nickel phosphides. In the case of Ni-P/SiO₂, the highest activity almost reaches 100%. While the optimal catalyst only reaches 57.8% for Ni-P/ γ -Al₂O₃. The HDN activity decreased with increasing calcination and reduction temperature for SiO₂-supported nickel phosphides. Obviously, in comparison with reduction temperature, calcination temperature exerts greater influence on catalytic HDN activity. For example, the HDN conversion of Ni-P₄₄₀/SiO₂ drops from 99.2% to 96.4% as the reduction temperature increased. The HDN conversion drops from 99.2% to 83.8% with increasing the calcination temperature for Ni-P⁵⁶⁰/SiO₂. In the case of Ni-P/

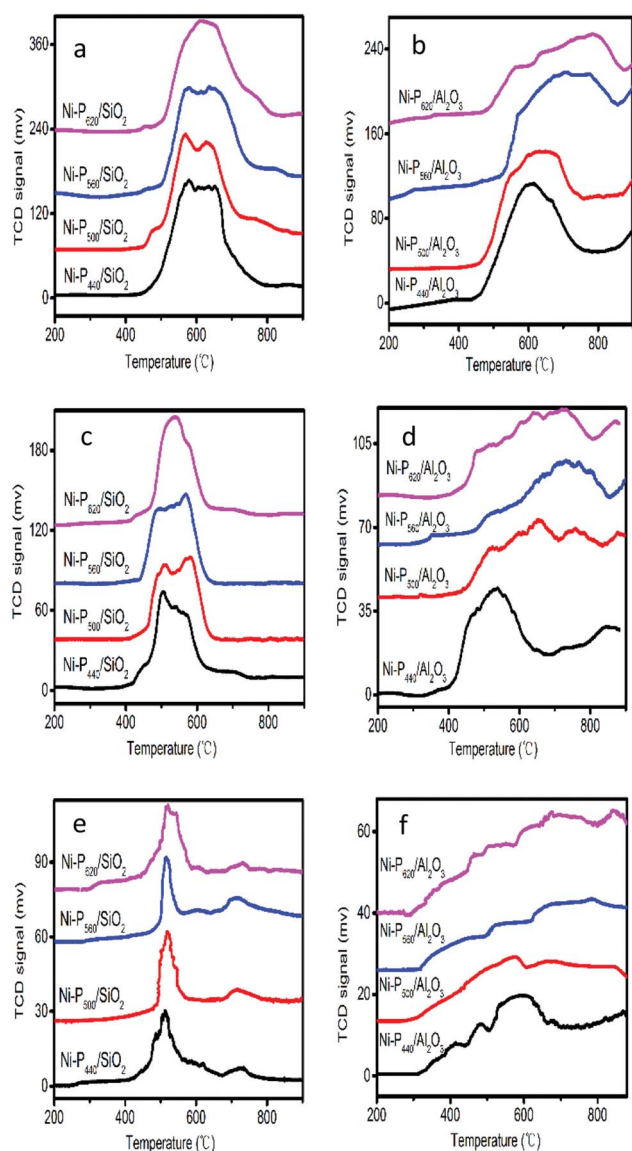


Fig. 2 H₂-TPR patterns of different SiO₂-supported nickel phosphides at heating rate of (a) 10 °C min⁻¹, (c) 3 °C min⁻¹, (e) 1 °C min⁻¹ and different γ -Al₂O₃-supported nickel phosphides at heating rate of (b) 10 °C min⁻¹, (d) 3 °C min⁻¹, (f) 1 °C min⁻¹.

Table 2 Quinoline HDN conversion, TOF, and *k* of different (a) SiO₂-supported nickel phosphides and (b) γ -Al₂O₃-supported nickel phosphides

Samples	HDN _C (%)	TOF (h ⁻¹)	<i>k</i> (mol kg ⁻¹ h ⁻¹)
Ni-P ₄₄₀ /SiO ₂	99.4	2.14	0.40
Ni-P ₅₀₀ /SiO ₂	95.3	2.05	0.24
Ni-P ₅₆₀ /SiO ₂	89.1	1.98	0.17
Ni-P ₆₂₀ /SiO ₂	81.4	1.96	0.13
Ni-P ₄₄₀ ⁶⁵⁰ /SiO ₂	98.6	4.02	0.33
Ni-P ₅₀₀ ⁶⁵⁰ /SiO ₂	93.7	4.02	0.21
Ni-P ₅₆₀ ⁶⁵⁰ /SiO ₂	86.7	3.74	0.16
Ni-P ₆₂₀ ⁶⁵⁰ /SiO ₂	83.2	3.78	0.14
Ni-P ₄₄₀ ⁷⁵⁰ /SiO ₂	96.4	4.66	0.26
Ni-P ₅₀₀ ⁷⁵⁰ /SiO ₂	91.3	4.42	0.19
Ni-P ₅₆₀ ⁷⁵⁰ /SiO ₂	79.3	4.38	0.13
Ni-P ₆₂₀ ⁷⁵⁰ /SiO ₂	78.3	4.33	0.12
Ni-P ₄₄₀ ⁵⁶⁰ /Al ₂ O ₃	16.9	0.075	0.014
Ni-P ₅₀₀ ⁵⁶⁰ /Al ₂ O ₃	15.6	0.067	0.013
Ni-P ₅₆₀ ⁵⁶⁰ /Al ₂ O ₃	14.7	0.068	0.012
Ni-P ₆₂₀ ⁵⁶⁰ /Al ₂ O ₃	12.8	0.061	0.011
Ni-P ₄₄₀ ⁶⁵⁰ /Al ₂ O ₃	33.5	0.214	0.032
Ni-P ₅₀₀ ⁶⁵⁰ /Al ₂ O ₃	32.3	0.211	0.031
Ni-P ₅₆₀ ⁶⁵⁰ /Al ₂ O ₃	31.9	0.208	0.030
Ni-P ₆₂₀ ⁶⁵⁰ /Al ₂ O ₃	31.6	0.209	0.029
Ni-P ₄₄₀ ⁷⁵⁰ /Al ₂ O ₃	58.6	0.720	0.068
Ni-P ₅₀₀ ⁷⁵⁰ /Al ₂ O ₃	57.3	0.715	0.066
Ni-P ₅₆₀ ⁷⁵⁰ /Al ₂ O ₃	54.3	0.700	0.061
Ni-P ₆₂₀ ⁷⁵⁰ /Al ₂ O ₃	52.1	0.695	0.057



γ -Al₂O₃, the variation tendency of HDN activity is not same as Ni-P/SiO₂. High calcination temperature is adverse to the catalyst, resulting in drop of the HDN conversion. While in contrast to Ni-P/SiO₂, high reduction temperature promotes the HDN activity of Ni-P/ γ -Al₂O₃. In addition, reduction temperature imposes greater influence on catalytic HDN activity. For example, the HDN activity of Ni-P₄₄₀/Al₂O₃ was improved from 16.9% to 57.8% as the reduction temperature increased. The HDN conversion drops from 16.9% to 12.8% with increasing the calcination temperature for Ni-P⁵⁶⁰/Al₂O₃.

The particle size tends to aggravate and becomes larger with increasing the calcination temperature for SiO₂-supported and Al₂O₃-supported nickel phosphides, leading to less exposure of active site. Here, the result of CO titration proved this. The CO uptake amount decreased with increasing the calcination temperature. In theory, HRTEM characterization can also find the difference resulted from calcination temperature. However, the distribution of catalyst particle is wide and the statistical result is not accurate (see Fig. S2†). For the sample with certain calcination temperature, the catalytic activity declined as the reduction temperature increased. According to H₂-TPR characterization of heating rate of 1 °C min⁻¹, it was found that the reduction of catalyst was nearly completed at 560 °C. Therefore, high reduction temperature not only no longer promotes the reducibility but also facilitates the growth of particle. In the case of Ni-P/ γ -Al₂O₃, the opposite tendency was observed compared with Ni-P/SiO₂. The HDN conversion dramatically increased with the reduction temperature. From H₂-TPR characterization of heating rate of 1 °C min⁻¹, the reduction still occurs beyond 750 °C. From XRD characterization, only Ni₁₂P₅ was produced at 560 °C, which was not as active as Ni₂P.²⁰ As reduction temperature increased, highly active Ni₂P was generated. Up to 750 °C, the predominant crystal phase was Ni₂P instead of Ni₁₂P₅. It should be mentioned that the H₂-TPR of heating rate of 1 °C min⁻¹ explicitly explain the different phenomena for the two sets of catalysts. While the usual characterization method with heating rate of 3, 10 °C min⁻¹ or others, it could not provide the accurate information.

The effect of calcination temperature on HDN of Ni-P/SiO₂ is more evident in comparison with Ni-P/ γ -Al₂O₃. It is considered that the interaction of SiO₂ with nickel phosphides is weaker than γ -Al₂O₃ with nickel phosphides. This cause aggravate of nickel phosphide particle with elevating the calcination temperature, leading to the decrease of HDN active site.

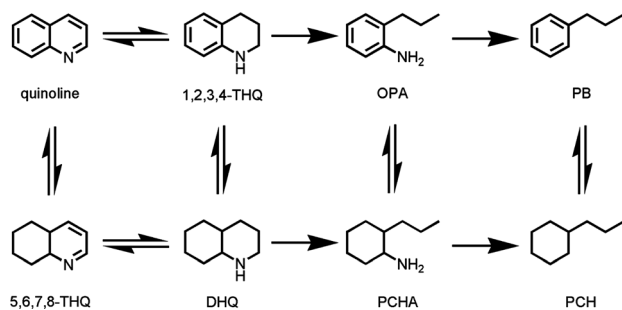
The TOF numbers of various catalysts at different calcination and reduction temperatures are calculated and presented in Table 2. For both SiO₂ and Al₂O₃-supported catalysts, TOFs were decreased with increasing the calcination temperature at certain reduction temperatures. Furthermore, TOFs increase with reduction temperature. However, the increasing extent was quite different. For example, for SiO₂-supported catalysts, the TOFs of Ni-P₄₄₀⁷⁵⁰/SiO₂ was almost twice as much as that of Ni-P₄₄₀⁵⁶⁰/SiO₂. While for Al₂O₃-supported catalyst, the TOFs of Ni-P₄₄₀⁷⁵⁰/Al₂O₃ was nearly 10 times as much Ni-P₄₄₀⁵⁶⁰/Al₂O₃. Many researchers reported that the active phase for both HDS and HDN is Ni₂P. According to XRD, for Ni-P⁵⁶⁰/Al₂O₃ the crystal phase was Ni₁₂P₅. But for Ni-P⁷⁵⁰/Al₂O₃, the main crystal phase was Ni₂P. This results in considerable difference between Ni-P⁵⁶⁰/Al₂O₃ and Ni-P⁷⁵⁰/Al₂O₃. Overall, the rate constants the rate constants exhibited similarly tendency with TOF numbers (Table 2).

Prior to the cleavage of the carbon–nitrogen bond of quinoline, hydrogenation of heterocyclic has to be finished owing to the high carbon–nitrogen bond strength. There are mainly several products, including PCH, PB, DHQ, THQ₁ and THQ₅ (Table 3). A little amount of Q was detected due to the equilibrium with THQ₁ and THQ₅.²¹ PCHA and PCHE was not detected due to the easily denitrogenation, hydrogenation and isomerization over nickel phosphides.²² The content of OPA was little, suggesting that the further reaction rate of OPA is faster than its formation rate. It is obvious that the predominant denitrogenation products is PCH rather than PB, which is similar to the result reported by Oyama *et al.*²³ Perot, G. and Ho, T. C. reported that the reaction of OPA is inhibited by THQ₁, Q and other nitrogen-containing compounds, resulting in the intrinsically unfavorable of denitrogenation *via* OPA to PB.^{21,24} According to the reaction network in Scheme 1, there

Table 3 Product distribution of quinoline HDN catalyzed over different calcination and reduction catalysts

Samples	Q	THQ ₁	THQ ₅	DHQ	OPA	PB	PCH	PB/PCH
Ni-P ₄₄₀ ⁵⁶⁰ /SiO ₂	0	0.14	0.28	0.37	0	7.09	92.13	0.0769
Ni-P ₅₀₀ ⁵⁶⁰ /SiO ₂	0.06	1.21	0.49	2.76	0.36	6.95	88.17	0.0788
Ni-P ₅₆₀ ⁵⁶⁰ /SiO ₂	0.08	3.47	1.54	7.41	0.32	6.47	80.72	0.0801
Ni-P ₆₂₀ ⁵⁶⁰ /SiO ₂	0.12	6.27	2.47	9.31	0.51	6.38	74.94	0.0851
Ni-P ₄₄₀ ⁷⁵⁰ /Al ₂ O ₃	0.26	13.72	3.58	23.13	1.51	3.47	54.34	0.0638
Ni-P ₅₀₀ ⁷⁵⁰ /Al ₂ O ₃	0.15	13.51	4.17	23.84	1.43	3.37	53.53	0.0629
Ni-P ₅₆₀ ⁷⁵⁰ /Al ₂ O ₃	0.09	14.46	4.31	24.89	1.46	3.41	51.38	0.0663
Ni-P ₆₂₀ ⁷⁵⁰ /Al ₂ O ₃	0.23	15.18	4.19	24.71	1.39	3.59	50.71	0.0709
Ni-P ₄₄₀ ⁶⁵⁰ /SiO ₂	0.06	0.42	0.27	0.56	0.07	7.28	91.32	0.0797
Ni-P ₅₀₀ ⁶⁵⁰ /SiO ₂	0.12	1.27	0.93	3.84	0.14	6.86	86.84	0.0790
Ni-P ₅₆₀ ⁶⁵⁰ /SiO ₂	0.08	4.14	1.43	7.36	0.27	6.59	80.12	0.0822
Ni-P ₆₂₀ ⁶⁵⁰ /SiO ₂	0.18	4.69	1.37	10.32	0.24	6.73	76.47	0.0871
Ni-P ₄₄₀ ⁷⁵⁰ /SiO ₂	0.07	1.36	0.64	1.39	0.17	7.16	89.23	0.0802
Ni-P ₅₀₀ ⁷⁵⁰ /SiO ₂	0.06	4.24	1.02	6.13	0.23	6.89	81.42	0.0816
Ni-P ₅₆₀ ⁷⁵⁰ /SiO ₂	0.18	4.63	2.41	13.14	0.36	6.12	73.16	0.0837
Ni-P ₆₂₀ ⁷⁵⁰ /SiO ₂	0.14	5.63	2.63	12.98	0.32	6.35	71.93	0.0882





Scheme 1 HDN reaction network of quinoline.

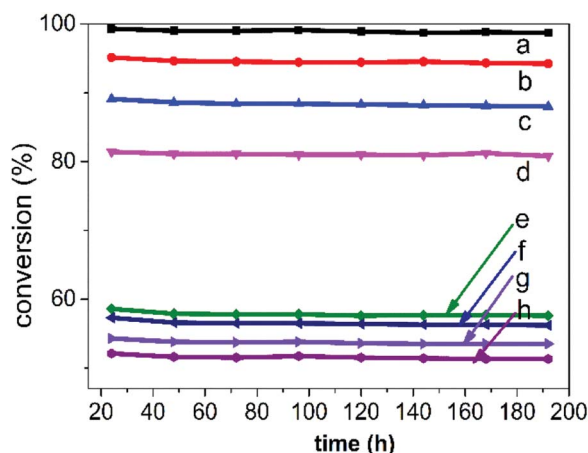


Fig. 3 HDN_C of quinoline as a function of time. a, b, c, d, e, f, g and h represents Ni-P₄₄₀⁵⁶⁰/SiO₂, Ni-P₅₀₀⁵⁶⁰/SiO₂, Ni-P₅₆₀⁵⁶⁰/SiO₂, Ni-P₆₂₀⁵⁶⁰/SiO₂, Ni-P₄₄₀⁷⁵⁰/Al₂O₃, Ni-P₅₀₀⁷⁵⁰/Al₂O₃, Ni-P₅₆₀⁷⁵⁰/Al₂O₃, Ni-P₆₂₀⁷⁵⁰/Al₂O₃, respectively.

are mainly two HDN pathways, *via* OPA or *via* DHQ. For the first path of OPA, hydrogenation of OPA to PCHA is the rate determining step. For the second path of DHQ, the rate determining step is C–N bond cleavage of DHQ to PCHA. According to the product distribution of Table 3, the ratio of PB to PCH was all slightly increased with the calcination temperature at certain reduction temperature. It is considered that two reasons give rise to this result. From CO uptakes, the number of active sites decreased as the calcination temperature was increased, resulting in decline of hydrogenation activity of OPA to PCHA. Furthermore, the number of Bronsted acidity was also declined with increasing the calcination temperature (Table S3†). Bronsted acid could promote the C–N bond cleavage of PCHA. The Bronsted acid site was produced by hydroxyl group of phosphide. However, high calcination temperature causes condensation of hydroxyl group, resulting in decrease of Bronsted acidity.

HDN reaction network of quinoline. Stability of Ni-P_x⁵⁶⁰/SiO₂ and Ni-P_x⁷⁵⁰/Al₂O₃ ($x = 440, 500, 560, 620$) were examined and the products were analysed in 24 h intervals for 192 h. The results were presented in Fig. 3. Overallly, there is little decline of catalytic activity during examined period, indicating the promising industrial perspective for this kind of catalyst. In fact, the HDN_C of Ni-P₄₄₀⁵⁶⁰/SiO₂, Ni-P₅₀₀⁵⁶⁰/SiO₂, Ni-P₅₆₀⁵⁶⁰/

SiO₂, Ni-P₆₂₀⁵⁶⁰/SiO₂ catalysts falls 0.7, 0.9, 1.2, 0.7% in 192 h, respectively. The Ni-P₄₄₀⁷⁵⁰/Al₂O₃, Ni-P₅₀₀⁷⁵⁰/Al₂O₃, Ni-P₅₆₀⁷⁵⁰/Al₂O₃, Ni-P₆₂₀⁷⁵⁰/Al₂O₃ catalysts drops 1.7, 1.5, 1.9, 1.4% in 192 h, respectively. Although no evident drops were observed for both two set of catalysts, there were still some difference between them. It is considered that more coke deposition happened over Al₂O₃-supported catalysts, resulting in cover of active sites. The deactivation by coke is related to catalyst acidity, which the Al₂O₃-supported catalysts have higher amount of acidity than the SiO₂-supported catalysts from Py-IR results.

Conclusions

In comparison with γ -Al₂O₃-supported nickel phosphides, highly HDN active phase of Ni₂P was formed on SiO₂-supported nickel phosphides at lower reduction temperature.

From H₂-TPR, the peak was shifted towards lower temperature with decreasing the heating rate. The SiO₂-supported nickel phosphides were reduced absolutely at 560 °C. The reduction was still performed beyond 750 °C for γ -Al₂O₃-supported nickel phosphides.

The quinoline HDN active sites and conversion was reduced when the reduction temperature surpassed 560 °C for nickel phosphides supported on SiO₂. While the quinoline HDN active sites and conversion dramatically increased with increasing the reduction temperature for nickel phosphides supported on γ -Al₂O₃.

Conflicts of interest

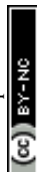
There are no conflicts to declare.

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References

- 1 S. T. Oyama and Y. K. Lee, *J. Phys. Chem. B*, 2005, **109**, 2109–2119.
- 2 Y. Y. Shu, Y. K. Lee and S. T. Oyama, *J. Catal.*, 2005, **236**, 112–121.
- 3 S. De, J. Zhang, R. Luque and N. Yan, *Energy Environ. Sci.*, 2016, **9**, 3314–3347.
- 4 P. Liu and J. A. Rodriguez, *J. Am. Chem. Soc.*, 2005, **127**, 14871–14878.
- 5 P. Liu, J. A. Rodriguez, T. Asakura, J. Gomes and K. Nakamura, *J. Phys. Chem. B*, 2005, **109**, 4575–4583.
- 6 M. Lu, A. Wang, X. Li, X. Duan, Y. Teng, Y. Wang, C. Song and Y. Hu, *Energy Fuels*, 2007, **21**, 554–560.
- 7 L. Zhang, W. Fu, Q. Yu, T. Tang, Y. Zhao, H. Zhao and Y. Li, *J. Catal.*, 2016, **338**, 210–221.



- 8 S. J. Sawhill, K. A. Layman, D. R. Van Wyk, M. H. Engelhard, C. Wang and M. E. Bussell, *J. Catal.*, 2005, **231**, 300–313.
- 9 A. I. d'Aquino, S. J. Danforth, T. R. Clinkingbeard, B. Ilic, L. Pullan, M. A. Reynolds, B. D. Murray and M. E. Bussell, *J. Catal.*, 2016, **335**, 204–214.
- 10 S. F. Yang, C. H. Liang and R. Prins, *J. Catal.*, 2006, **237**, 118–130.
- 11 V. T. da Silva, L. A. Sousa, R. M. Amorim, L. Andrini, S. J. A. Figueroa, F. G. Requejo and F. C. Vicentini, *J. Catal.*, 2011, **279**, 88–102.
- 12 W. Wang, X. Li, Z. C. Sun, A. J. Wang, Y. Y. Liu, Y. Y. Chen and X. P. Duan, *Appl. Catal., A*, 2016, **509**, 45–51.
- 13 A. L. Imbault and K. J. Smith, *Catal. Lett.*, 2016, **146**, 1886–1891.
- 14 J. Chen, S. Zhou, D. Ci, J. Zhang, R. Wang and J. Zhang, *Ind. Eng. Chem. Res.*, 2009, **48**, 3812–3819.
- 15 J. X. Chen, Y. Chen, Q. Yang, K. L. Li and C. C. Yao, *Catal. Commun.*, 2010, **11**, 571–575.
- 16 J. A. Rodriguez, J. Y. Kim, J. C. Hanson, S. J. Sawhill and M. E. Bussell, *J. Phys. Chem. B*, 2003, **107**, 6276–6285.
- 17 T. I. Koranyi, A. E. Coumans, E. J. M. Hensen, R. Ryoo, H. S. Kim, E. Pfeifer and Z. Kasztovszky, *Appl. Catal., A*, 2009, **365**, 48–54.
- 18 V. H. J. Debeer, G. C. A. Schuit, T. h. Van sintf, A. c. Van haand, M. W. J. Wolfs, J. F. Engelen and C. H. Amberg, *J. Catal.*, 1972, **27**, 357–363.
- 19 P. A. Clark and S. T. Oyama, *J. Catal.*, 2003, **218**, 78–87.
- 20 S. T. Oyama, X. Wang, Y. K. Lee, K. Bando and F. G. Requejo, *J. Catal.*, 2002, **210**, 207–217.
- 21 G. Perot, *Catal. Today*, 1991, 447–472.
- 22 M. Lu, A. Wang, X. Li, X. Duan, Y. Teng, Y. Wang, C. Song and Y. Hu, *Energy Fuels*, 2007, **21**, 554–560.
- 23 S. T. Oyama, X. Wang, Y. K. Lee and W. J. Chun, *J. Catal.*, 2004, **221**, 263–273.
- 24 T. C. Ho, *Catal. Rev.: Sci. Eng.*, 1988, **30**, 117–160.

