



Preparation and Hydrodenitrogenation Performance of Ni₂P/TiO₂-Al₂O₃ Catalyst

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TiO₂-Al₂O₃ composite support was prepared by the sol-gel process and then was used to prepare the precursors in oxidation state of Ni₂P/TiO₂-Al₂O₃ catalysts through wet impregnation method. The Ni₂P/TiO₂-Al₂O₃ catalyst was obtained *via in situ* hydrogen reduction technique in a fixed-bed reactor and its hydrodenitrogenation activity was tested using quinoline as model compound. Results showed that TiO₂/Al₂O₃ molar ratios had a significant influence on hydrodenitrogenation activity as well as the loading of Ni₂P. Catalyst exhibited the best catalytic activity when n(TiO₂):n(Al₂O₃) was 1/4 and the loading of Ni₂P was 25 wt % and its hydrodenitrogenation rate could reach 98.2 %.

Key Words: Nickel phosphide, Hydrodenitrogenation, Wet impregnation, Quinoline.

INTRODUCTION

With the crude oil becoming more poorer in quality and the world regulations for environmental protection more stringent, the requirements of clean fuel production can not be satisfied by using the method of hydrodesulfurization (HDS) and hydrodenitrification (HDN) with conventional sulfide catalysts. The legislation that has been introduced over past years in many parts of the world demands very low sulfur levels in fuels¹. Because of these urgent needs for lowering the sulfur level, improvements of the industrial hydrodesulfurization and hydrodenitrification processes have been ongoing for many years².

The transition metal phosphide had a superior hydrodesulfurization and hydrodenitrification activity and a better stability than the traditional sulfide catalysts had been reported^{3,4}. Loading the Ni₂P on a carrier with larger specific surface area is needed⁵, as the specific surface area of the unloaded Ni₂P is less than 1 m²/g. Though the literature had reported the preparation of different Ni₂P catalysts with the same metal loading supported on activated carbon⁶, MCM-41⁷, SiO₂⁸, Al₂O₃⁹ and TiO₂¹⁰, the application of the composite support in hydrofining of the phosphide was less reported. The TiO₂-Al₂O₃ composite support¹¹⁻¹³ which has been proved has a larger specific surface area¹⁴, larger pore volume, more concentrated pore distribution¹⁵ and also higher selectivity than traditional Al₂O₃ carrier, is used widely.

In this study, Ni₂P/TiO₂-Al₂O₃ catalyst was used as the object of research, to investigate the influence of carrier and

the loading of active component on the structure of the catalyst and the hydrodenitrification activity.

EXPERIMENTAL

Nickel nitrate, ammonium dihydrogen phosphate, cetyl trimethyl ammonium bromide, absolute ethyl alcohol, hydrochloric acid, glacial acetic acid (analytically pure); tetrabutyl titanate (chemical pure); alumina (industrial grade); deionized water (own product).

Electric Blast Drying Oven, type HG101-1, produced by Nanjing experimental instrument factory; box-type resistance furnace, type SX-4-10, produced by Shenyang electric furnace enterprise; numerical show precise power mixer, type JJ-1, Jiangsu chengxixiaoyang electronic instruments factory; metering pump, series II, produced by SSI/LabAlliance America; Rigaku x-ray diffractometer, type D/M AX-2500, Rigaku Corporation Japan; Nicolet Impact 410 infrared spectrometer, produced by Nico let company.

TiO₂-Al₂O₃ composite support: First, dissolved a certain amount of tetrabutyl titanate into the absolute ethyl alcohol and then the glacial acetic acid was added dropwise into the solution prepared before as inhibitor, while stirring. By doing this, the glacial acetic acid could form stable chelate with tetrabutyl titanate, hydrolyzed uniformly, reduced the reunion of the hydrolyzate and then a kind of colloidal solution with small and uniform particle size was obtained. Added the mixture of absolute ethyl alcohol, deionized water and hydrochloric acid into the colloidal solution drop by drop, then stir and serve. After that, the cetyltrimethylammonium bromide

(CTAB) which was used as the sole template, was added slowly to the mixture mixed well before, to make sure that the colloidal particles formed an open-framework. Meanwhile, added Al_2O_3 into the colloidal solution slowly, stirring for 2 h and standing for 24 h at room temperature and the colloidal sol lost mobility gradually and formed rigid gels. Put the rigid gels into the electric drum wind drying oven, in which the water, organic group and solvent inside the rigid gels could be removed after drying at $120\text{ }^\circ\text{C}$ for 24 h. Put the crystal prepared with the above steps into muffle furnace, calcinated it up from room temperature to $550\text{ }^\circ\text{C}$ in the method of temperature programming (at the rate of $25\text{ }^\circ\text{C}/15\text{ min}$) and stayed for 4 h at this temperature, then the $\text{TiO}_2\text{-Al}_2\text{O}_3$ composite support was obtained.

Preparation of catalyst

Bulk Ni_2P : Bulk Ni_2P , used as reference, was prepared following a two-step procedure¹⁶. In the first step, a certain volume of $\text{NH}_4\text{H}_2\text{PO}_4$ solution was added to the same volume of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ solution that was maintained under magnetic stirring. The mixed solution was dissolved after the addition of nitric acid to adjust the pH value and then dried and calcined, resulting in a ling brown solid, which will be referred to herein as $\text{Ni}_x\text{P}_y\text{O}_z$. In the second step, $\text{Ni}_x\text{P}_y\text{O}_z$ was reduced to Ni_2P by TPR.

Preparation of precursor: The $\text{TiO}_2\text{-Al}_2\text{O}_3$ composite support was impregnated using the incipient wetness method by means of a solution resulting from the mixing of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ dissolved by the deionized water (determine water absorption of the carrier in advanced). The amounts of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ were calculated to achieve the mole ratio $n_{\text{Ni}}/n_{\text{P}} = 2/1.3$ and the loading was calculated by Ni_2P . After 2 h of impregnation at room temperature, 12 h of drying at $120\text{ }^\circ\text{C}$ and 4 h of calcinating at $550\text{ }^\circ\text{C}$ using the method of temperature programming (at the rate of $25\text{ }^\circ\text{C}/15\text{ min}$), the precursor of $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ catalyst could be obtained finally.

In situ reduction: The hydrodenitration of quinoline was carried out using a fixed-bed pressure micro-reactor. Prior to hydrodenitration reaction, the oxidic precursors of the phosphides were transformed into the active phases using an *in situ* H_2 TPR method. The precursor of $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ was pelleted, crushed and sieved to 20-40 meshes. A total of 10 mL precursor was putted into the reaction tube. The precursor was reduced in a 100 mL/min H_2 flow by heating from room temperature to $120\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C}/\text{min}$ and holding at $120\text{ }^\circ\text{C}$ for 1 h, then from 120 to $400\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C}/\text{min}$ and holding at $400\text{ }^\circ\text{C}$ for 1 h, eventually from 400 - $550\text{ }^\circ\text{C}$ at $2\text{ }^\circ\text{C}/\text{min}$ and holding at $550\text{ }^\circ\text{C}$ for 150 min. Then the reactor was cooled to the hydrodenitration reaction temperature ($300\text{ }^\circ\text{C}$) to gain the final catalyst of $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$.

Characterization of catalyst: The XRD diffractograms of the composite support and the catalyst, either in passivated or in oxidic form were obtained in a Rigaku D/MAX 2500 diffractometer operated at 40kV and 30mA, using nickel-filtered $\text{CuK}\alpha$ monochromatized radiation. The scanning rate is $6^\circ/\text{min}$ and scanning range is $2\theta = 10\text{-}8^\circ$. The Fourier transform infrared (FT-IR) spectra were collected on a Nicolet-Impact 410 Spectrometer, which used KBr as the supporter of

the structure of samples and the vibration of the framework and the samples were recorded.

Evaluation hydrodenitration activity: The hydrodenitration activities of the catalysts were investigated using an undecane solution containing 1 wt % quinoline as the model compound in the fixed-bed pressure micro-reactor. The operating condition of the reactor were reaction temperature $300\text{-}360\text{ }^\circ\text{C}$, total H_2 pressure 3 MPa, hydrogen-oil ratio 500 (v/v) and LHSV 3 h^{-1} . Emptied the hydrodenitration products after 3 h achieved the steady reaction condition and then took samples after another 1 h. Liquid samples were collected at an interval of 0.5 h. The nitrogen removal ratio of the sample that could show the activity of the catalyst was analyzed by a gas chromatographs equipped with an FID detector using commercial HP-5 column.

RESULTS AND DISCUSSION

The XRD patterns of $\text{TiO}_2\text{-Al}_2\text{O}_3$ composite support with different mole ratio of $\text{TiO}_2/\text{Al}_2\text{O}_3$ are shown in Fig. 1. Compared to JCPDS, XRD diffractograms of the sample presented broad and sharp characteristic peaks of anatase at $2\theta = 25.4^\circ$, 37.8° , 47.8° , 54.7° and 63.8° tending to be perfect¹⁷, indicating that TiO_2 and Al_2O_3 existed, respectively in the anatase and the $\gamma\text{-Al}_2\text{O}_3$ crystal structure. As the mole ratio of $\text{TiO}_2/\text{Al}_2\text{O}_3$ decreased, the characteristic peaks of TiO_2 (anatase) decreased and that of Al_2O_3 increased.

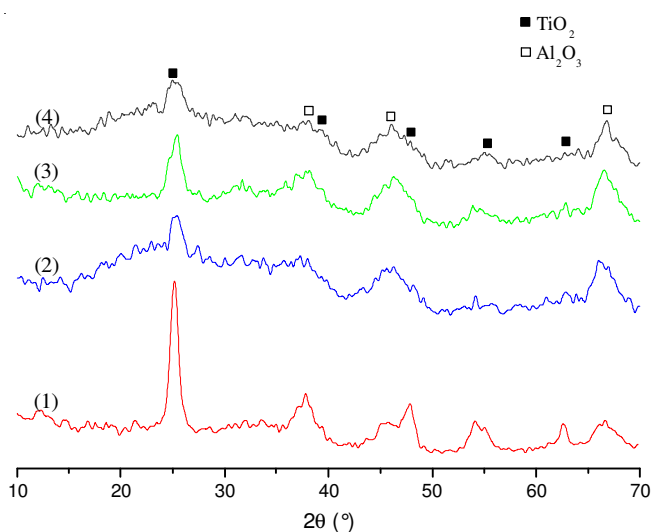


Fig. 1. XRD patterns of $\text{TiO}_2\text{-Al}_2\text{O}_3$ with different mole ratios of $\text{TiO}_2/\text{Al}_2\text{O}_3$: (1)-1:2; (2)-1:4; (3)-1:6; (4)-1:8; ■ TiO_2 ; □ Al_2O_3

Fig. 2 shows the XRD diffractograms of the catalyst with different loading of Ni_2P under the condition that mole ratio of $\text{TiO}_2/\text{Al}_2\text{O}_3$ was 1:4. The diffraction patterns of the $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ show a combination of the individual characteristics of both $\text{TiO}_2\text{-Al}_2\text{O}_3$ and bulk Ni_2P . Fig. 2 suggested that when the loading of Ni_2P was 10 %, the characteristic peaks of Ni_2P were not observed, because that the Ni_2P was fully dispersed on the carrier surface and pore structure. When the loading reached 15 %, the characteristic peaks of Ni_2P could have been found out with a smooth peak pattern, indicating Ni_2P has existed in the catalyst in single crystal phase, just less in amount. When the loading got to 15 %, the characteristic

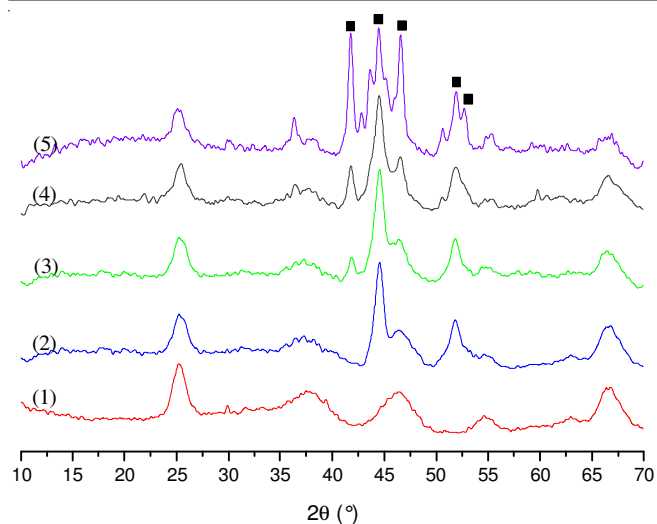


Fig. 2. XRD patterns of Ni₂P/TiO₂-Al₂O₃ with different loadings of Ni₂P: (1)-0; (2)-10 %; (3)-15 %; (4)-25 %; (5)-35 %; ■- Ni₂P

peaks of Ni₂P were obviously presented at the peaks of $2\theta = 40.7^\circ$, 44.6° and 47.3° , suggesting that the amount of Ni₂P single crystal phase increased obviously, and the phase coexisted between Ni₂P and TiO₂-Al₂O₃.

The FT-IR patterns of TiO₂-Al₂O₃ composite support with different mole ratios are shown in Fig. 3. The spectra shows the following bands: the absorption peak at 495 cm^{-1} caused by the vibration of Ti-O-Ti bond inside TiO₂ shifted and became stronger gradually, with the increase in mole ratio of TiO₂/Al₂O₃, for the reason that the rearrangement of A³⁺ and particle effected the vibration of Ti-O-Ti bond, suggesting the existence in the carrier of Ti-O-Al bond; the broad peaks at $700\text{-}900\text{ cm}^{-1}$ in the spectra is associated with the vibration of four-coordinated AlO₄ and the intensity of the band that obviously weakened by the decrease of mole ratio of TiO₂/Al₂O₃, exhibited that TiO₂ could reduce the four-coordinated A³⁺ above the surface of γ -Al₂O₃, while the coordinated and unsaturated four-coordinated A³⁺ was the very activity site of the strong interactions between γ -Al₂O₃ carrier and the metal component it supported.

So, the strong interactions between Ni₂P and γ -Al₂O₃ could be weakened by introducing TiO₂ into γ -Al₂O₃ to inhibit the generation of AlPO₄^{17,18}.

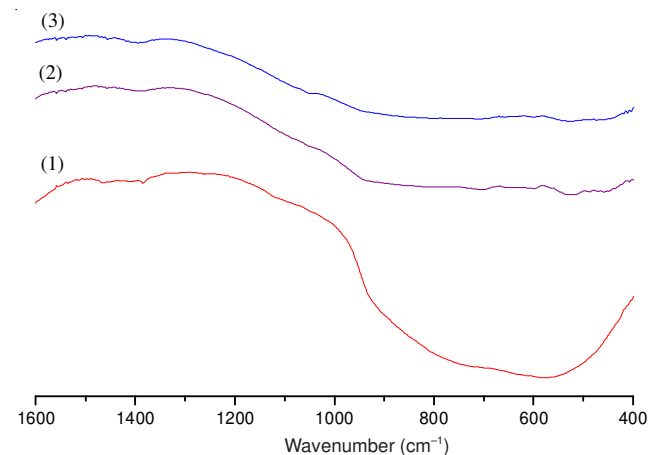


Fig. 3. FT-IR spectra of TiO₂-Al₂O₃ with different mole ratios of TiO₂/Al₂O₃: (1)-1:2; (2)-1:6; (3)-1:8

Catalytic performance in the quinoline solution hydrodenitrogenation reaction (expressed by nitrogen removal ratio) at 360°C , total H₂ pressure 3 MPa, hydrogen-oil ratio 500 (v/v) and LHSV 3 h⁻¹ for the Ni₂P/TiO₂, Ni₂P/Al₂O₃, Ni₂P/TiO₂-ZrO₂ and Ni₂P/TiO₂-Al₂O₃ samples is presented in Table-1. The hydrodenitrogenation activities of Ni₂P/TiO₂-ZrO₂ and Ni₂P/TiO₂-Al₂O₃ were about the same but much higher than that of Ni₂P/TiO₂ and Ni₂P/Al₂O₃. Moreover, the Ni₂P/TiO₂-ZrO₂ catalyst got a relatively lower activity compared to Ni₂P/TiO₂-Al₂O₃. Because TiO₂-Al₂O₃ carrier owned a higher surface area, pore volume and pore distributions¹⁵ that could increase the number of the effective sites and promoted the hydrodenitrogenation activity of the catalyst.

TABLE-1
HDN ACTIVITY OF CATALYSTS
SUPPORTED ON DIFFERENT CARRIERS

Catalyst	HDN conversion (%)	Catalyst	HDN conversion (%)
Ni ₂ P/TiO ₂	62.4	Ni ₂ P/TiO ₂ -ZrO ₂	93.5
Ni ₂ P/Al ₂ O ₃	70.3	Ni ₂ P/TiO ₂ -Al ₂ O ₃	98.2

Fig. 4 shows the hydrodenitrogenation conversion of quinoline as a function of temperature on the Ni₂P/TiO₂-Al₂O₃ catalysts with different mole ratios of TiO₂/Al₂O₃. The operating conditions were the same as the former. It can be seen from Fig. 4 that the hydrodenitrogenation conversion for each catalyst increased with temperature and the mole ratio of TiO₂/Al₂O₃ had a noteworthy effect on hydrodenitrogenation activity. In particular, when n(TiO₂):n(Al₂O₃) was 1:4 the catalyst displayed the highest activity in the temperature range investigated. When Ni₂P was loaded on pure TiO₂ or TiO₂/Al₂O₃ composite carrier but that n(TiO₂):n(Al₂O₃) was 1:2, 1:6 and 1:8, the hydrodenitrogenation activity decreased significantly. This could be attributed to that the crystal structure, surface area and pore structure of the composite carrier affected the catalyst hydrodenitrogenation activity directly. With the parameter of n(TiO₂):n(Al₂O₃) = 1:4, the catalyst existed chiefly in anatase TiO₂ state revealed higher hydrodenitrogenation activity. Reports⁴ have shown that TiO₂ has a function of electronic accelerator for hydrodenitrogenation catalyst and

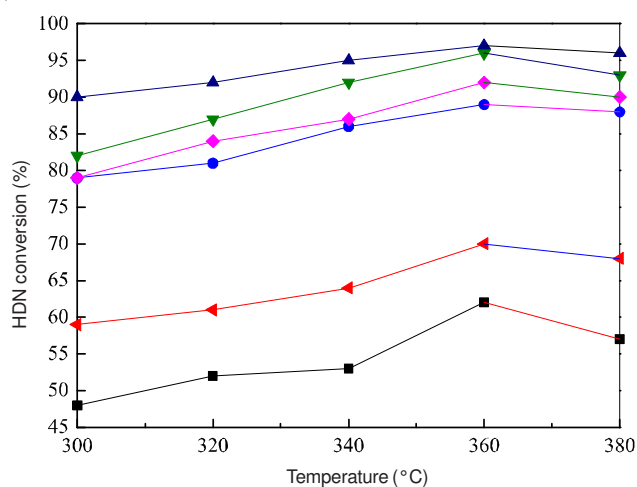


Fig. 4. Hydrodenitrogenation conversion as a function of temperature over Ni₂P/TiO₂-Al₂O₃ with different mole ratios of TiO₂/Al₂O₃: ■- TiO₂; ●-1:2; ▲-1:4; ▼-1:6; ◆-1:8; ◀- Al₂O₃

has synergy with Ni₂P, that could enhance the ability of C-N bond cleavage of Ni₂P. The reasons might be that Ti³⁺ formed during the reaction and then the electron in Ti³⁺ was transferred to Ni₂P, increased the electron density of Ni₂P that is helpful for C-N bond cleavage¹⁹, additional, promote the hydrodenitration activity of Ni₂P.

The phosphatized Ni was used as an active ingredient in the catalyst and the influence of different loading of Ni₂P on hydrodenitration activity was investigated at the condition that n(TiO₂):n(Al₂O₃) was 1:4 and n(Ni):n(P) was 2:1.3. Fig. 5 shows the hydrodenitration conversion of quinoline as a function of temperature on the Ni₂P/TiO₂-Al₂O₃ catalysts with 10, 15, 25 and 35 % loading of Ni₂P. As indicated in Fig. 5, hydrodenitration activity increased greatly with increasing loading of Ni₂P, resulting from the great relations with the dispersing capacity (threshold value) of the active ingredients above TiO₂-Al₂O₃ composite carrier. Maximum hydrodenitration activity was observed at a Ni₂P loading of 25 %, whereas the 10, 15 and 35 % loading suffered a low activity. This is due to that when the loading was 10 %, on account of the little number of active ingredients Ni₂P was completely put into the channel of composite carrier, even could not overlay the surface of the carrier, leading to the decrease of the active sites in catalyst; when it was 15 %, though a certain number of active ingredients appeared on the surface and in the channel of the composite carrier, the dispersing capacity (threshold value) of Ni₂P on such supporter hadn't been reached, so the activity could have got a step further. When the loading reached 25 %, Ni₂P got its threshold value. On the other words, the active ingredients got its maximum overlay on the catalyst and formed the largest number of the hydrodenitration active sites, resulting in the maximum hydrodenitration activity; that the loading of 35 % exceeded the threshold value of Ni₂P, so Ni₂P existed mainly as a monomer rather than dispersing layer, whose hydrodenitration activity was higher, led to the decrease of hydrodenitration activity of the catalyst.

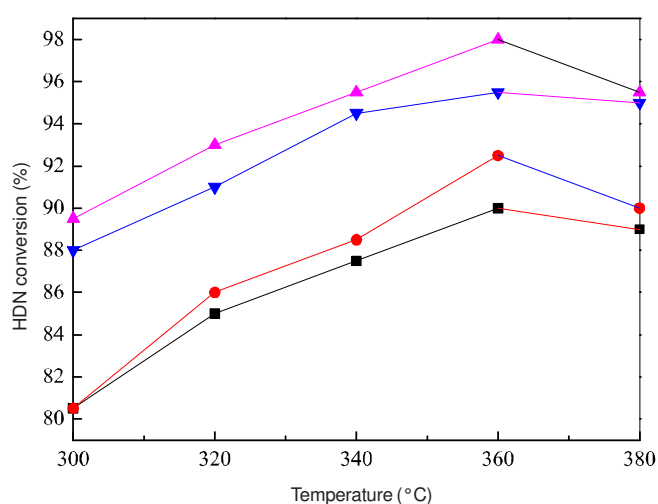


Fig. 5. Hydrodenitration conversion as a function of temperature over Ni₂P/TiO₂-Al₂O₃ with different loadings of Ni₂P: ■-10 %; ●-15 %; ▲-25 %; ▼-35 %

Conclusion

XRD results indicated that TiO₂ existed in the form of anatase in the composite support and its characteristic peaks were broad and sharp, tending to be perfect. FT-IR results revealed that addition of TiO₂ to γ -Al₂O₃ weakened the strong interaction between Ni₂P and γ -Al₂O₃ and then inhibited the generation of AlPO₄ on surface. The mole ratios of (TiO₂)/(Al₂O₃) had a great influence on hydrodenitration activity of TiO₂-Al₂O₃ composite carrier and when n(TiO₂):n(Al₂O₃) = 1:4, the highest activity will be attained. The loading of effected greatly on catalyst activity. When the Ni₂P loading got to 25 %, the catalyst pore and surface are all loaded with active ingredients, leading to the maximum activity of the catalyst.

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