Preparation and Hydrodenitrogenation Performance of $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ Catalyst

JINGRU ZHANG, HAIYAN WANG* and MIN WEI

College of Petrochemical Engineering, Liaoning University of Petroleum Chemical Technology, Fushun 113001, P.R. China

*Corresponding author: Tel: +86 13941336296; E-mail: fswhy@163.com

(Received: 11 April 2013;

Accepted: 28 October 2013)

AJC-14304

$\text{TiO}_2\text{-Al}_2\text{O}_3$ composite support was prepared by the sol-gel process and then was used to prepare the precursors in oxidation state of $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ catalysts through wet impregnation method. The $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{TiO}_2/\text{Al}_2\text{O}_3$ molar ratios had a significant influence on hydrodenitrogenation activity as well as the loading of Ni_2P . Catalyst exhibited the best catalytic activity when $n(\text{TiO}_2):n(\text{Al}_2\text{O}_3)$ was 1/4 and the loading of Ni_2P 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 Ni_2P on a carrier with larger specific surface area is needed⁵, as the specific surface area of the unloaded Ni_2P is less than $1 \text{ m}^2/\text{g}$. Though the literature had reported the preparation of different Ni_2P catalysts with the same metal loading supported on activated carbon⁶, MCM-41⁷, SiO_2 ⁸, Al_2O_3 ⁹ and TiO_2 ¹⁰, the application of the composite support in hydrofining of the phosphide was less reported. The $\text{TiO}_2\text{-Al}_2\text{O}_3$ 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 Al_2O_3 carrier, is used widely.

In this study, $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ 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, seriesII, 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.

$\text{TiO}_2\text{-Al}_2\text{O}_3$ 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 °C for 24 h. Put the crystal prepared with the above steps into muffle furnace, calcinated it up from room temperature to 550 °C in the method of temperature programming (at the rate of 25 °C/15 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 °C and 4 h of calcinating at 550 °C using the method of temperature programming (at the rate of 25 °C/15 min), the precursor of $\text{Ni}_2\text{P/TiO}_2\text{-Al}_2\text{O}_3$ catalyst could be obtained finally.

In situ reduction: The hydrodenitrification of quinoline was carried out using a fixed-bed pressure micro-reactor. Prior to hydrodenitrification reaction, the oxidic precursors of the phosphides were transformed into the active phases using an *in situ* H_2 TPR method. The precursor of $\text{Ni}_2\text{P/TiO}_2\text{-Al}_2\text{O}_3$ 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 °C at 5 °C/min and holding at 120 °C for 1 h, then from 120 to 400 °C at 5 °C/min and holding at 400 °C for 1 h, eventually from 400-550 °C at 2 °C/min and holding at 550 °C for 150 min. Then the reactor was cooled to the hydrodenitrification reaction temperature (300 °C) to gain the final catalyst of $\text{Ni}_2\text{P/TiO}_2\text{-Al}_2\text{O}_3$.

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°/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 hydrodenitrification activity: The hydrodenitrification 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 300-360 °C, total H_2 pressure 3 MPa, hydrogen-oil ratio 500 (v/v) and LHSV 3 h^{-1} . Emptied the hydrodenitrification 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 $\text{Ni}_2\text{P/TiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ with different loadings of Ni_2P : (1)-0; (2)-10 %; (3)-15 %; (4)-25 %; (5)-35 %; ■- Ni_2P

peaks of Ni_2P were obviously presented at the peaks of $2\theta = 40.7^\circ$, 44.6° and 47.3° , suggesting that the amount of Ni_2P single crystal phase increased obviously, and the phase coexisted between Ni_2P and $\text{TiO}_2\text{-Al}_2\text{O}_3$.

The FT-IR patterns of $\text{TiO}_2\text{-Al}_2\text{O}_3$ 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 TiO_2 shifted and became stronger gradually, with the increase in mole ratio of $\text{TiO}_2/\text{Al}_2\text{O}_3$, for the reason that the rearrangement of Al^{3+} 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 AlO_4 and the intensity of the band that obviously weakened by the decrease of mole ratio of $\text{TiO}_2/\text{Al}_2\text{O}_3$, exhibited that TiO_2 could reduce the four-coordinated Al^{3+} above the surface of $\gamma\text{-Al}_2\text{O}_3$, while the coordinated and unsaturated four-coordinated Al^{3+} was the very activity site of the strong interactions between $\gamma\text{-Al}_2\text{O}_3$ carrier and the metal component it supported.

So, the strong interactions between Ni_2P and $\gamma\text{-Al}_2\text{O}_3$ could be weakened by introducing TiO_2 into $\gamma\text{-Al}_2\text{O}_3$ to inhibit the generation of AlPO_4 ^{17,18}.

Fig. 3. FT-IR spectra 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)-1:6; (3)-1:8

Catalytic performance in the quinoline solution hydrodenitrogenation reaction (expressed by nitrogen removal ratio) at 360°C , total H_2 pressure 3 MPa, hydrogen-oil ratio 500 (v/v) and LHSV 3 h^{-1} for the $\text{Ni}_2\text{P}/\text{TiO}_2$, $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$, $\text{Ni}_2\text{P}/\text{TiO}_2\text{-ZrO}_2$ and $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ samples is presented in Table-1. The hydrodenitrogenation activities of $\text{Ni}_2\text{P}/\text{TiO}_2\text{-ZrO}_2$ and $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ were about the same but much higher than that of $\text{Ni}_2\text{P}/\text{TiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$. Moreover, the $\text{Ni}_2\text{P}/\text{TiO}_2\text{-ZrO}_2$ catalyst got a relatively lower activity compared to $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$. Because $\text{TiO}_2\text{-Al}_2\text{O}_3$ 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 (%)
$\text{Ni}_2\text{P}/\text{TiO}_2$	62.4	$\text{Ni}_2\text{P}/\text{TiO}_2\text{-ZrO}_2$	93.5
$\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$	70.3	$\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$	98.2

Fig. 4 shows the hydrodenitrogenation conversion of quinoline as a function of temperature on the $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ catalysts with different mole ratios of $\text{TiO}_2/\text{Al}_2\text{O}_3$. 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 $\text{TiO}_2/\text{Al}_2\text{O}_3$ had a noteworthy effect on hydrodenitrogenation activity. In particular, when $n(\text{TiO}_2):n(\text{Al}_2\text{O}_3)$ was 1:4 the catalyst displayed the highest activity in the temperature range investigated. When Ni_2P was loaded on pure TiO_2 or $\text{TiO}_2/\text{Al}_2\text{O}_3$ composite carrier but that $n(\text{TiO}_2):n(\text{Al}_2\text{O}_3)$ 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 $n(\text{TiO}_2):n(\text{Al}_2\text{O}_3) = 1:4$, the catalyst existed chiefly in anatase TiO_2 state revealed higher hydrodenitrogenation activity. Reports⁴ have shown that TiO_2 has a function of electronic accelerator for hydrodenitrogenation catalyst and

Fig. 4. Hydrodenitrogenation conversion as a function of temperature over $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ with different mole ratios of $\text{TiO}_2/\text{Al}_2\text{O}_3$: ■- TiO_2 ; ●-1:2; ▲-1:4; ▼-1:6; ◆-1:8; ◀- Al_2O_3

has synergy with Ni_2P , that could enhance the ability of C-N bond cleavage of Ni_2P . The reasons might be that Ti^{3+} formed during the reaction and then the electron in Ti^{3+} was transferred to Ni_2P , increased the electron density of Ni_2P that is helpful for C-N bond cleavage¹⁹, additional, promote the hydrodenitrification activity of Ni_2P .

The phosphatized Ni was used as an active ingredient in the catalyst and the influence of different loading of Ni_2P on hydrodenitrification activity was investigated at the condition that $n(\text{TiO}_2):n(\text{Al}_2\text{O}_3)$ was 1:4 and $n(\text{Ni}):n(\text{P})$ was 2:1.3. Fig. 5 shows the hydrodenitrification conversion of quinoline as a function of temperature on the $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ catalysts with 10, 15, 25 and 35 % loading of Ni_2P . As indicated in Fig. 5, hydrodenitrification activity increased greatly with increasing loading of Ni_2P , resulting from the great relations with the dispersing capacity (threshold value) of the active ingredients above $\text{TiO}_2\text{-Al}_2\text{O}_3$ composite carrier. Maximum hydrodenitrification activity was observed at a Ni_2P 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 Ni_2P 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 Ni_2P on such supporter hadn't been reached, so the activity could have got a step further. When the loading reached 25 %, Ni_2P 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 hydrodenitrification active sites, resulting in the maximum hydrodenitrification activity; that the loading of 35 % exceeded the threshold value of Ni_2P , so Ni_2P existed mainly as a monomer rather than dispersing layer, whose hydrodenitrification activity was higher, led to the decrease of hydrodenitrification activity of the catalyst.

Fig. 5. Hydrodenitrification conversion as a function of temperature over $\text{Ni}_2\text{P}/\text{TiO}_2\text{-Al}_2\text{O}_3$ with different loadings of Ni_2P : ■-10 %; ●-15 %; ▲-25 %; ▼-35 %

Conclusion

XRD results indicated that TiO_2 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 TiO_2 to $\gamma\text{-Al}_2\text{O}_3$ weakened the strong interaction between Ni_2P and $\gamma\text{-Al}_2\text{O}_3$ and then inhibited the generation of AlPO_4 on surface. The mole ratios of $(\text{TiO}_2)/(\text{Al}_2\text{O}_3)$ had a great influence on hydrodenitrification activity of $\text{TiO}_2\text{-Al}_2\text{O}_3$ composite carrier and when $n(\text{TiO}_2):n(\text{Al}_2\text{O}_3) = 1:4$, the highest activity will be attained. The loading of effected greatly on catalyst activity. When the Ni_2P loading got to 25 %, the catalyst pore and surface are all loaded with active ingredients, leading to the maximum activity of the catalyst.

REFERENCES

1. R. Prins and M.E. Bussell, *Catal. Lett.*, **142**, 1413 (2012).
2. B. Pawelec, R.M. Navarro, J.M. Campos-Martin and J.L.G. Fierro, *Catal. Sci. Technol.*, **1**, 23 (2012).
3. Y.Q. Wang, M.Sc. Thesis, Nanjing University of Technology, Nan Jing (2004).
4. M.H. Lu, M.Sc. Thesis, Dalian University of Technology, Da Lian (2007).
5. D.Y. Li, X.Z. Yu and C.L. Chen, *J. Chem. Eng. Chin. Univ.*, **20**, 826 (2006).
6. Y. Shu and S.T. Oyama, *Carbon*, **43**, 1517 (2005).
7. A.J. Wang, L.F. Ruan, Y. Teng, X. Li, M. Lu, J. Ren, Y. Wang and Y. Hu, *J. Catal.*, **229**, 314 (2005).
8. L.H. Liu, G.C. Li and Y.Q. Liu, *Petrol. Proc. Petrochem.*, **42**, 20 (2011).
9. S.J. Sawhill, K.A. Layman, D.R. Van Wyk, M. Engelhard, C. Wang and M. Bussell, *J. Catal.*, **231**, 300 (2005).
10. X.Z. Yu, Y.Q. Wang and C.L. Chen, *J. Fuel Chem. Technol.*, **34**, 100 (2006).
11. J.B. Hu, W. Li, M.H. Zhang and N.J. Guan, *Inorg. Chem.*, **20**, 587 (2005).
12. Y. Wei and X.X. Liu, *Petrochemical Technol.*, **35**, 173 (2006).
13. S. Damyanova, A. Spojakina and K. Jiratova, *Appl. Catal. A*, **125**, 257 (1995).
14. J. Rame, L. Cedeno and G.J. Buscan, *Catalysis*, **184**, 59 (1999).
15. Y. Shi, *Acta Petrolei Sin. (Petroleum Processing Sec.)*, **21**, 13 (2005).
16. X. Wang, P. Clark and S.T. Oyama, *J. Catal.*, **208**, 321 (2002).
17. L.M. Song, W. Li and M.H. Zhang, *Chin. J. Catal.*, **28**, 144 (2007).
18. H. Song, J. Yang, J. Zhao and L. Chou, *Chin. J. Catal.*, **31**, 449 (2010).
19. X.P. Duan, X. Li, A. Wang, Y. Teng, Y. Wang and Y. Hu, *Catal. Today*, **149**, 11 (2010).