Asian Journal of Chemistry Vol. 22, No. 6 (2010), 4439-4449

Alumina Supported $H_3PW_{12}O_{40}$ and Ni Catalysts for Hydrocracking of *n*-Decane

JINGYUN SHENG, BO QIU, HAO JIN, XIAODONG YI* and WEIPING FANG*
Department of Chemistry, State Key Laboratory for Physical Chemistry of the Solid Surfaces,
College of Chemistry and Chemical Engineering, Xiamen University, Xiamen-361005, P.R. China
Tel/Fax: (86)(592)2186291; E-mail: xdyi@xmu.edu.cn; wpfang@xmu.edu.cn

A novel series of bifunctional Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts for the hydrocracking of *n*-decane were designed and prepared. The evaluation results of these novel catalysts showed that they possessed extremely high catalytic activity for hydrocracking of *n*-decane and excellent tolerance to the sulfur and nitrogen compounds in the feedstock. In order to reveal the structure and nature of the catalysts, a number of characterizations including XRD, BET, H_2-TPD, NH_3-TPD and FT-IR of pyridine adsorption were carried out. The characterization results demonstrated that the high catalytic activity and high C_5^+ selectivity of the catalysts can be attributed to the unique structure of the $H_3PW_{12}O_{40}$ and the interactions between the metal sites and the $H_3PW_{12}O_{40}$.

Key Words: Hydrocracking, Bifunctional catalyst, Hydrogen spillover, $H_3PW_{12}O_{40}$, Decane.

INTRODUCTION

In recent years, in order to minimize the environmental impact of automotive fuels, the need of high-quality diesel fuels has been always increasing. High-pressure hydrocracking is a catalytic refining process to produce clean fuels by removing sulfur, nitrogen and metals from the heavy petroleum fractions[1-3]. Obviously, this technique which ensures the elimination of sulfur and nitrogen-containing compounds as well as a deep saturation of aromatics will be more and more important in the near future[1,4].

Bifunctional catalysts, which consist of highly dispersed group VI and VIII metals were widely used in refining processes, such as hydrocracking and hydroisomerization. These bifunctional catalysts can be used for hydrogenation or dehydrogenation. They also act as acidic supports for cracking or isomerization of some feedstocks. In particular, metal catalysts supported on zeolites have received great attention for their high catalytic activities[5-7]. The strong acidity of zeolites favours successive cracking reactions of the feed molecules with formation of the desired light products[8]. However, it is well known that zeolites can be easily poisoned by nitrogen-containing compounds or polycyclic aromatic compounds[6,7]. Also, due to zeolites' small pore size, the access to active sites is restricted to only small feed molecules. In order to solve these problems, great effort has been devoted to the searching for a good support with large pore size and suitable acidity.

Heteropolyacids was a type of environmentally friendly solid acid catalysts. They can offer several advantages in terms of catalytic performance, strong acid and redox sites[9] and have been used in some reactions. $H_3PW_{12}O_{40}$ is one polyoxotungstate[9] made up of heteropoly anions. It has a basic structural unit of metal-oxygen octahedral and our group has recently demonstrated that reduced Ni-$H_3PW_{12}O_{40}$/SiO_2 catalysts exhibited great activities for the hydrocracking of decane under several conditions[10].

The aim of present work is to develop novel hydrocracking catalysts which contained $H_3PW_{12}O_{40}$ as the acid sites and Ni as the metal sites. Alumina was selected here as the support of these catalysts because of its suitable pore size, surface area and great stability. $H_3PW_{12}O_{40}$ might help to offer the adequate acidity in the alumina.

These novel Ni-$H_3PW_{12}O_{40}$/Al_2O_3 catalysts showed excellent performances. They not only had high activities for hydrocracking of *n*-decane, but also had good tolerances to the sulfur and nitrogen compounds in the feedstock. The Ni-$H_3PW_{12}O_{40}$/Al_2O_3 catalysts were thoroughly characterized by BET, XRD, H_2-TPD and Py-IR and the relations of their high catalytic activities with the hydro-dehydro function and the surface acidic properties were discussed in details.

EXPERIMENTAL

The Ni/Al_2O_3 catalysts were prepared by impregnation of alumina support (commercial product, specific surface area 270 m^2 g^{-1}) within a solution containing the desired quantities of $Ni(NO_3)_2$. Impregnated samples were dried overnight at 120 °C and then calcined in air at 400 °C for 3 h.

The Ni-$H_3PW_{12}O_{40}$/Al_2O_3 catalysts were prepared by impregnation of Ni/Al_2O_3 catalysts within a solution containing the desired quantities of $H_3PW_{12}O_{40}$. After impregnation, samples were dried in air overnight at 120 °C without calcination.

n-Decane used in the present study is commercially available reagent without any further purification. To study the poisoning resistance of the reduced catalysts to organic sulfur and nitrogen compounds, *n*-decane with 750 ppm of thiophene and 500 ppm of pyridine were also used as the feedstock. Prior to the reaction, all the catalysts were reduced in a flow of H_2 at 300 °C for 1 h or sulfided at 300 °C for 8 h using a flow of CS_2/H_2 (60 cm^3 min^{-1}, volume ratio 5/95). The catalytic performance of the catalysts was measured in a down flow fixed-bed quartz tube reactor cased in a stainless steel tube (i.d. = 8 mm; 150 cm in length) at 2 MPa, LHSV = 4 h^{-1} and H_2/*n*-decane volume ratio of 1500. The products were collected and analyzed after 4 h of reaction time. All products were separated by condensation. The gas products were analyzed by gas chromatography with a Porapak Q column (3 m) and a TCD detector and the liquid products were analyzed by an OV-101 capillary column (30 m) and a FID detector.

For comparison, a commercial hydrocracking catalyst disclosed in Chinese patent CN1393521 was also measured for hydrocracking under the same conditions.

The surface area (BET) and pore volume of the catalysts were determined by means of nitrogen adsorption at -194 °C on an adsorption automatic instrument (Micromeritics Tristar 3000). The samples were pretreated at 300 °C for 3 h in vacuum. Powder X-ray diffraction (XRD) characterization was carried out on a X' Pert Pro automatic powder diffractometer operated at 40 kV and 30 mA, using Cu Kα (λ = 0.15406 nm) monochromatized radiation in all cases. Each step of 0.0167° was measured for 10 s from 20-70° (2θ). JCPDS file database was used for peak identification. Temperature-programmed desorption of hydrogen (H_2-TPD) measurements were done in a Micromeritics AutoChem II 2920 analyzer. 0.2 g of catalyst sample was filled in a U-shaped quartz reactor tube and a thermocouple was placed onto the top of sample. All samples were pretreated in He (20 mL min^{-1}) at 400 °C for 2 h then in H_2 (20 mL min^{-1}) for 1 h. After cooling down to 50 °C, the samples were swept with helium for 60 min and finally the desorption step was performed from 50-700 °C at a heating rate of 10 °C min^{-1} and with 30 mL min^{-1} of helium total flow. Acid properties which were determined by ammonia temperature-programmed desorption (NH_3-TPD) were measured in a Micromeritics AutoChem II 2920 analyzer. 0.2 g of catalyst sample was filled in a U-shaped quartz reactor tube and a thermocouple was placed onto the top of sample. All samples were pretreated in He (20 mL min^{-1}) at 400 °C for 2 h then in H_2 (20 mL min^{-1}) for 1 h. After cooling down to 100 °C, 5 % NH_3/He was passed over the samples for 0.5 h. Then, the samples were swept with helium for 1 h and finally the desorption step was performed from 100-700 °C at a heating rate of 10 °C min^{-1} and 30 mL min^{-1} of helium total flow. The desorbed products were monitored by TCD and MS equipment simultaneously. FT-IR spectra were also used to evaluate the pyridine absorption on catalysts. In this experiment, the catalyst samples were pressed into self-supporting wafers and treated in H_2 at 300 °C in an IR cell for 1 h followed by evacuation at 300 °C for 5 min to remove the gas phase H_2. After cooling to 100 °C, the samples were exposed to pyridine vapour for 10 min. Then the spectra were recorded after evacuation at high temperatures. The IR spectra were recorded in the spectral range 1700-1400 cm^{-1} with 32 scans and at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Table-1 lists the specific surface areas measured by the BET method and the compositions of the catalysts without calcination. The surface area of the catalysts was found to decrease with the increase of $H_3PW_{12}O_{40}$ content and the decrease was even more pronounced for 5 % Ni-60 % $H_3PW_{12}O_{40}/Al_2O_3$ sample, perhaps due to pore blockage.

The XRD patterns of Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts without calcination are shown in Fig. 1. No diffraction peaks of NiO and $H_3PW_{12}O_{40}$ appeared for the catalysts with fixed amount of 5 % Ni. From the results, it is deduced that both of NiO and $H_3PW_{12}O_{40}$ were well dispersed onto the catalysts surface.

TABLE-1
COMPOSITION AND PHYSICAL PROPERTIES OF THE OXIDIZED CATALYSTS

Catalysts	Surface area (m^2 g^{-1})	Pore size (nm)	Ni (wt %)	$H_3PW_{12}O_{40}$ (wt %)
Al_2O_3	220	11.8	0	0
5 % Ni/Al_2O_3	216	11.0	5	0
50 % $H_3PW_{12}O_{40}$/Al_2O_3	148	6.6	0	50
5 % Ni-30 % $H_3PW_{12}O_{40}$/Al_2O_3	165	9.0	5	30
5 % Ni-40 % $H_3PW_{12}O_{40}$/Al_2O_3	141	8.0	5	40
5 % Ni-50 % $H_3PW_{12}O_{40}$/Al_2O_3	112	6.0	5	50
5 % Ni-60 % $H_3PW_{12}O_{40}$/Al_2O_3	64	5.0	5	60
Commercial catalyst	275	4.9	–	–

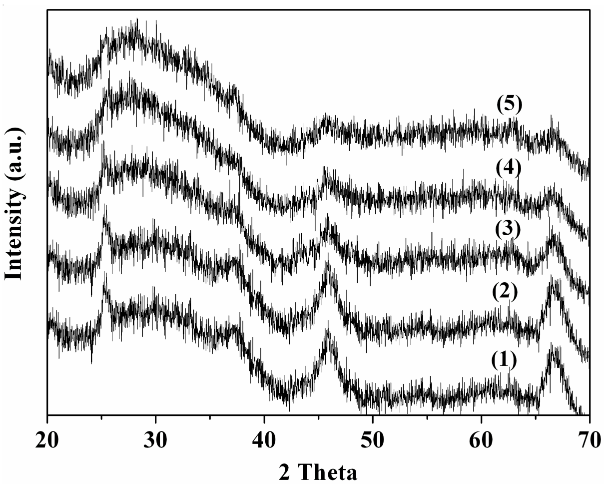

Fig.1. XRD patterns of Ni-$H_3PW_{12}O_{40}$/Al_2O_3 catalysts with the different contents of $H_3PW_{12}O_{40}$. (**1**) Al_2O_3 (**2**) 5 % Ni-30 % $H_3PW_{12}O_{40}$/Al_2O_3 (**3**) 5 % Ni-40 % $H_3PW_{12}O_{40}$/Al_2O_3 (**4**) 5 % Ni-50 % $H_3PW_{12}O_{40}$/Al_2O_3 (**5**) 5 % Ni-60 % $H_3PW_{12}O_{40}$/Al_2O_3

The evaluation results of the reduced and sulfided Ni-$H_3PW_{12}O_{40}$/Al_2O_3 catalysts with different Ni/$H_3PW_{12}O_{40}$ weight ratios for hydrocracking of *n*-decane were shown in Figs. 2a and 2b, wherein the conversion of *n*-decane and the yield of C_5^+ were used to demonstrate the activity of the catalyst and the selectivity of desired liquid products, respectively. For both of the reduced and sulfided 5 % Ni-$H_3PW_{12}O_{40}$/Al_2O_3 catalysts, when $H_3PW_{12}O_{40}$ content in the catalyst equals to 50 %, the conversions of *n*-decane reached maximum, while the activity of the reduced catalysts was found to be higher than that of the sulfided ones.

The activity of the Ni-$H_3PW_{12}O_{40}$/Al_2O_3 catalysts was found to increase with increasing the content of $H_3PW_{12}O_{40}$ in catalysts up to 50 %. This observation could be explained by the good balance between metal and acid sites achieved by tuning

$H_3PW_{12}O_{40}$ contents. On the other hand, it is found that the C_5^+ selectivity kept on decreasing with increasing the $H_3PW_{12}O_{40}$ contents. It might be due to the deep cracking which resulted from breaking of the balance between the acidic function and hydrogenation function after excess incorporation of $H_3PW_{12}O_{40}$.

To compare the catalytic performance of these catalysts with typical industrial catalysts, a commercial catalyst containing zeolites was also evaluated. The results showed that the reduced Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts exhibited a little lower activity than that of the reduced commercial catalyst, while the sulfided Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts showed much higher activity than the sulfided commercial catalyst. This interesting finding suggests that the poisoning resistance of Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts to sulfur is much better than that of commercial catalyst.

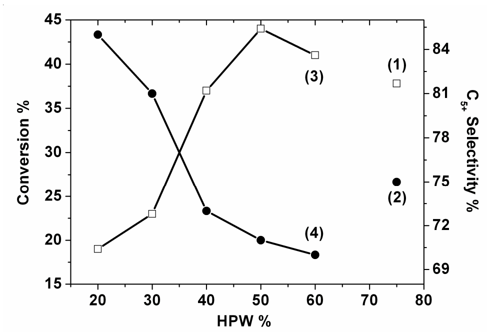

Fig. 2a. Comparison of different catalysts for hydrocracking of *n*-decane (**1**) Conversion over sulfided commercial catalyst; (**2**) C_5^+ selectivity over sulfided commercial catalyst; (**3**) Conversion over sulfided 5 % Ni-$H_3PW_{12}O_{40}/Al_2O_3$; (**4**) C_5^+ selectivity over sulfided 5 % Ni-$H_3PW_{12}O_{40}/Al_2O_3$ reaction conditions: T = 300 °C; H_2/decane = 1500; P = 2 Mpa and LHSV = 4 h^{-1}

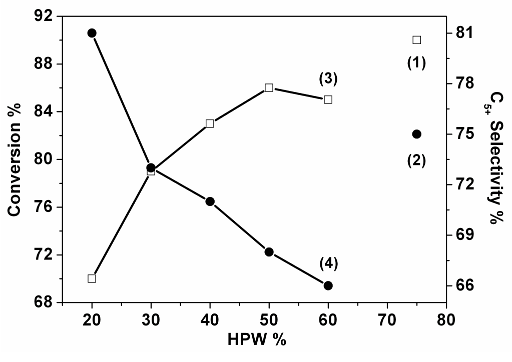

Fig. 2b. Comparison of different catalysts for hydrocracking of *n*-decane (**1**) Conversion over reduced commercial catalyst; (**2**) C_5^+ selectivity over reduced commercial catalyst; (**3**) Conversion over reduced 5 % Ni-$H_3PW_{12}O_{40}/Al_2O_3$; (**4**) C_5^+ selectivity over reduced 5 % Ni-$H_3PW_{12}O_{40}/Al_2O_3$ reaction conditions: T = 300 °C; H_2/decane = 1500; P = 2 Mpa and LHSV = 4 h^{-1}

Since the industrial feedstock always contain a small amount of heteroatoms (sulfur and nitrogen), the catalysts should have the ability to resist poisoning by these sulfur and nitrogen-containing impurities. To further investigate the poisoning resistance of the reduced Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts, small quantity of thiophene and pyridine were incorporated into *n*-decane to mimic the industrial feedstock. In Fig. 3, the catalytic performance of the reduced Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts for the mimicked industrial feedstock was compared with the reduced commercial catalyst. It is clear that both of these two catalysts had significantly worse catalytic performance. However, the activity of the reduced Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts was much higher than that of the reduced commercial catalyst, which confirmed that the reduced Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts had excellent poisoning resistances to sulfur and nitrogen-containing compound and had great potential as catalysts for practical industrial processes.

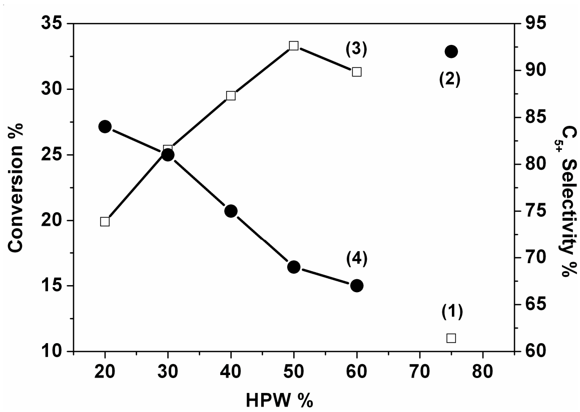

Fig. 3. Comparison of reduced catalysts for hydrocracking of *n*-decane with 750 ppm thiophene and 500 ppm pyridine (**1**) Conversion over reduced commercial catalyst; (**2**) C_5^+ selectivity over reduced commercial catalyst; (**3**) Conversion over reduced 5 % Ni-$H_3PW_{12}O_{40}/Al_2O_3$; (**4**) C_5^+ selectivity over reduced 5 % Ni-$H_3PW_{12}O_{40}/Al_2O_3$; reaction conditions: T = 300 °C; H_2/decane = 1500; P = 2 Mpa and LHSV = 4 h^{-1}

Many papers have proposed that sulfur poisoned the active metal sites, resulting in loss of hydrogenation activity; while nitrogen poisoned the acidic sites, also resulting in the activity loss[11,12]. Sulfur tolerance has been shown to be related to the formation of electron-deficient metal sites, which in turn weaken the strength of the sulfur-metal bond. In present work, it is suggested that the following mechanism for the exceptional performance of these catalysts. The elemental Ni is the hydro-dehydrogenation active site in these catalysts. It can dissociate the hydrogen molecules adsorbed to highly reactive hydrogen species (*i.e.*, H^+, H^-, $H^{\delta+}$)[13,14] or ion pairs. The heavy hydrocarbons, just as our feedstock, will be cracked at the acidic sites to produce unstable intermediates and these intermediates will react with the highly reactive hydrogen species to produce the stable products. Thus, the reaction is catalyzed. Furthermore, because of the hydrogen spillover, the catalyst surface is completely covered with a reactive hydrogen layer, which can effectively prevent the formation of sulfur-metal bonds and result in the better resistance to sulfur and nitrogen-containing compounds. Further studies about the hydrogen spillover will be discussed later with the H_2-TPD experiments.

It was mentioned that hydrocracking process is usually carried out using a metal/acid bifunctional catalyst, over which the alkanes are dehydrogenated-hydrogenated on metallic sites and then isomerized or cracked on the acid sites through classical or non-classical ion carbenium chemistry[15,16].

To examine the acidic property of the Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts, NH_3-TPD was carried out and the spectra are shown in Fig. 4. From Fig. 4 two desorption peaks of ammonia at 200 and 450 °C, respectively can be detected. As the amount of $H_3PW_{12}O_{40}$ increasing, the amount of NH_3 desorbed increases. The activity of 5 % Ni-60 % $H_3PW_{12}O_{40}/Al_2O_3$ catalyst is lower than that of 5 % Ni-50 % $H_3PW_{12}O_{40}/SiO_2$ catalyst, which might be due to the decrease of the surface areas with the increasing content of $H_3PW_{12}O_{40}$ on the catalysts or the unsuitable metal/acid ratio. It seems that the acidity of the catalyst may not simply account for the catalytic activity.

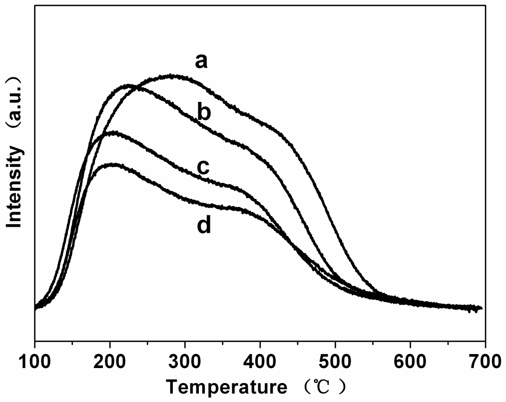

Fig. 4. NH_3-TPD profiles of reduced catalysts. (a) 5 % Ni-60 % $H_3PW_{12}O_{40}/Al_2O_3$; (b) 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$; (c) 5 % Ni-40 % $H_3PW_{12}O_{40}/Al_2O_3$; (d) 5 % Ni-30 % $H_3PW_{12}O_{40}/Al_2O_3$

In order to know the interaction of the metal Ni and $H_3PW_{12}O_{40}$ more clearly, FT-IR was used to characterize the nature of acid sites by pyridine absorption on very thin self-supporting films of Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts. The spectra of pyridine absorbed at 300 °C are shown in Fig. 5. The bands around 1450 cm^{-1} are typical of pyridine adsorbed at Lewis acid centers; while the bands around 1542 cm^{-1} are evidence for the formation of pyridinium cations resulting from adsorption at Bronsted acid sites[17]. The band around 1490 cm^{-1} contains contributions from

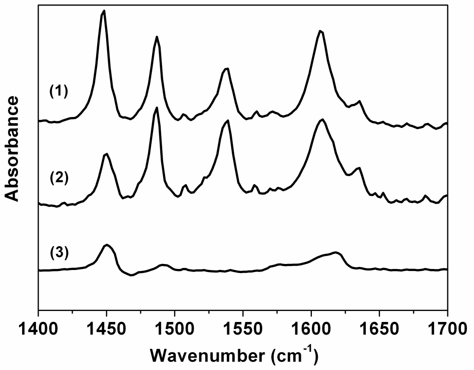

Fig. 5. FT-IR spectra of pyridine absorbed on reduced catalysts. (1) 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$; (2) 50 % $H_3PW_{12}O_{40}/Al_2O_3$; (3) 5 % Ni/Al_2O_3

both forms of adsorbed pyridine. For 5 % Ni/Al_2O_3 catalyst, only a low absorption bands for Lewis acid sites can be detected in the IR spectra, indicating an extremely weak acidity as expected. Both 50 % $H_3PW_{12}O_{40}/Al_2O_3$ sample and 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$ sample showed some certain acidity and the 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$ sample was found to bear stronger Lewis acidity than the 50 % $H_3PW_{12}O_{40}/Al_2O_3$ sample. These results demonstrated that some new Lewis acid sites were formed in the Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts after the nickel doping. That might be caused by the interaction between the metal sites and the acid sites, which produced some electron-deficient metal sites with strong Lewis acidity.

The metal properties of reduced Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts were studied by H_2-TPD (Fig. 6). The H_2-TPD profiles show that all the Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts exhibit two H_2 desorbed peaks at nearly 200 and 400 °C, respectively. The amount of H_2 desorbed in two temperature stage increase with the increasing of the amount of $H_3PW_{12}O_{40}$ in the catalysts.

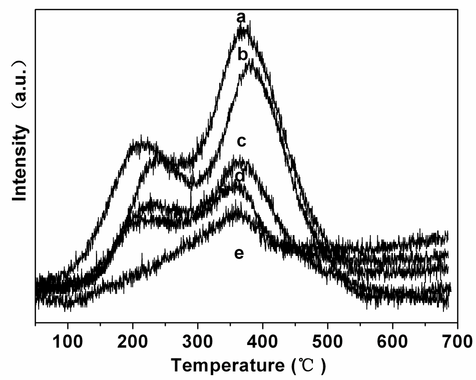

Fig. 6. H_2-TPD profiles of catalysts. (a) 5 % Ni-70 % $H_3PW_{12}O_{40}/Al_2O_3$; (b) 5 % Ni-60 % $H_3PW_{12}O_{40}/Al_2O_3$; (c) 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$; (d) 5 % Ni-40 % $H_3PW_{12}O_{40}/Al_2O_3$. (e) 5 % Ni-30 % $H_3PW_{12}O_{40}/Al_2O_3$

Three catalysts: 5 % Ni/Al_2O_3, 50 % $H_3PW_{12}O_{40}/Al_2O_3$ and 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$ were investigated and the results are shown in Fig. 7. The 5 % Ni/Al_2O_3 catalyst has only one H_2-absorbed stage at low temperature region and the 50 % $H_3PW_{12}O_{40}/Al_2O_3$ catalyst also has only one H_2-absorbed stage, but at higher temperature region. However, for the 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$ catalyst, two H_2 desorbed stages were noticed and the amount of H_2 absorbed was much more than the other two catalysts.

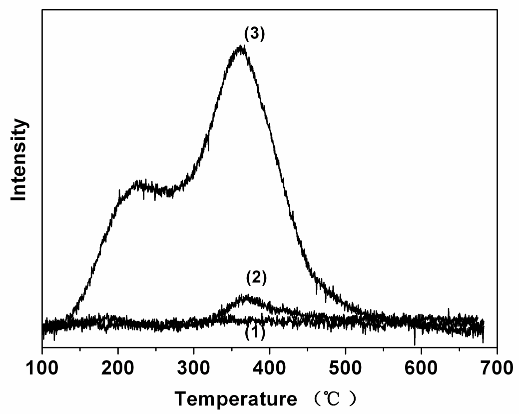

Fig. 7. H_2-TPD profiles of catalysts. (1) 5 % Ni/Al_2O_3; (2) 5 % /$H_3PW_{12}O_{40}/Al_2O_3$; (3) 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$

According to the classic bifunctional metal-acid mechanisms, the metal sites were involved in the initial alkane activation through dehydrogenation. These mechanisms successfully explained a number of experimental observations, but failed to account for the role of hydrogen and the synergy between these two catalyst components[18]. A non-classic bifunctional mechanism was also suggested, in which the activation of *n*-alkane reactant was done through a redox step[19].

In present studies, the increased amount of H_2 desorbed from the 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$ catalyst can be explained as follow: On one hand, the $H_3PW_{12}O_{40}$ can not only acted as the acid site, but also cooperate with the hydrogenation metal site to act as a potential hydrogen supply. On the other hand, taking into account of the results of the H_2-TPD experiment, that the amount of hydrogen absorded on the 5 % Ni-50 % $H_3PW_{12}O_{40}/Al_2O_3$ catalyst highly increased after the promoting the metal Ni on the 50 % $H_3PW_{12}O_{40}/Al_2O_3$ catalyst. The desorption trend of H_2 from the catalysts can be explained by the hydrogen spillover mechanism[13]. Spillover is only one mechanistic step in a sequence that can occur in adsorption. For hydrogen spillover, the adsorbed H_2 usually dissociated on the metal into atomic H or partially dissociated and even retain their molecule identity during spillover. Hydrogen spillover species can then move across the metal surface to the interface with the $H_3PW_{12}O_{40}$ or the support. And then the species can diffuse across the whole surface of catalysts including the non-adsorbing surface.

Based on all the above discussions, we can draw the conclusion that the spillover hydrogen enhanced the hydro-dehydro function of the catalysts, which accounts for the great activity of the catalysts for hydrocracking. This conclusion was already proved by previous report[10]. On the other hand, the reaction evaluations presented above are well correlated to the TPD studies of the catalysts. Hydrogen was at first absorbed and dissociated on the metal Ni to produce highly reactive hydrogen species, which spilled over to not only acidic site but also support. With the reactive hydrogen layer covering which can prevent the formation of the metal-S, the catalyst surface was able to remain clean and active in the whole process. Consequently, the activity and the resistance to the sulfur and nitrogen compounds of catalysts for hydrocracking will be enhanced.

Conclusion

A novel group of bifunctional Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts has been prepared and showed high activity for *n*-decane hydrocracking. For both the reduced and sulfided 5 % Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts, when $H_3PW_{12}O_{40}$ contents in the catalyst equaled to 50 %, the conversions of *n*-decane reached the maximum. Moreover, in the presence of nitrogen and sulfur-containing compounds in the feedstock, the activity of the reduced 5 % Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts was much higher than that of commercial catalyst. The high activity and exceptional resistance to sulfur and nitrogen compounds of Ni-$H_3PW_{12}O_{40}/Al_2O_3$ catalysts for hydrocracking was most probably attribute to the unique structure of the $H_3PW_{12}O_{40}$, which not only acted as an acid site, but also cooperated with the hydrogenation metal site to act as a potential hydrogen supply. The hydrogen spilled over not only acidic site but also support. Hence, the catalyst surface always owned a reactive hydrogen layer covering which can prevent the formation of the metal-S and remained to be clean. Consequently, the activity and the resistance to the sulfur and nitrogen compounds of catalysts for hydrocracking will be enhanced.

ACKNOWLEDGEMENT

This project is supported by the Ministry of Science and Technology of China (2004CB217805, 2010CB226903).

REFERENCES

1. M. Roussel, J.L. Lemberton, M. Guisnet, T. Cseri and E. Benazzi, *J. Catal.*, **218**, 427 (2003).
2. A. Corma, *Catal. Lett.*, **22**, 33 (1993).
3. A. Hennico, A. Billon, P.H. Bigeard and J.P. Peries, *Rev. Inst. Français. Petrol.*, **48**, 127 (1993).
4. J.K. Minderhoud, J.A.R. Van. Veen and A.P. Hagan, *Stud. Surf. Sci. Catal.*, **127**, 3 (1999).
5. G.M. Kumaran, S. Gatg, M. Kumar, N. Viswanatham, J.K. Gupta, L.D. Sharma and G.M. Dhar, *Energy Fuel*s, **20**, 2308 (2006).
6. S.P. Elangovan, C. Bischof and M. Hartmann, *Catal. Lett.*, **80**, 35 (2002).
7. L. Yang, J. Li, X.D. Yuan, J. Shen and Y.T. Qi, *J. Mol. Catal. A: Chem.*, **262**, 114 (2007).
8. M. Misono, *Chem. Commun.*, 1141 (2001).
9. H. Firouzabadi, N. Iranpoor and K. Amani, *Green Chem.*, **3**, 131 (2001).
10. B. Qiu, X.D. Yi, L. Lin, W.P. Fang and H.L. Wan, *Catal. Today*, **131**, 464 (2008).

11. D. Eliche-Quesada, J.M. Mérida-Robles, E. Rodríguez-Castellon and A. Jiménez-Lopez, *Appl. Cata. B: Environ.*, **65**, 118 (2006).
12. M. Roussel, S. Norsic, J.-L. Lemberton, M. Guisnet, T. Cseri and E. Benazzi, *Appl. Catal. A: Gen*., **279**, 53 (2005).
13. M.M. Hossain, *Chem. Eng. J.*, **123**, 15 (2006).
14. V.M. Benitez, J.C. Yori, J.M. Grau, C.L. Pieck and C.R. Vera, *Energy Fuel*s, **20**, 422 (2006).
15. K. Fang, W. Wei, J. Ren and Y. Sun, *Catal. Lett*., **93**, 235 (2004).
16. S.T. Sie, *Ind. Eng. Chem. Res*., **32**, 403 (1993).
17. K. Sato and Y. Iwata, *Catal. Today*, **45**, 367 (1998).
18. S. Kuba, P. Lukinskas, R.K. Grasselli, B.C. Gates and H. Knozinger, *J. Catal*., **216**, 353 (2003).
19. A. Martinez, G. Prieto, M.A. Arribas and P. Concepción, *Appl. Catal. A: Gen*., **309**, 224 (2006).

(*Received*: 20 August 2009; *Accepted*: 12 February 2010) AJC-8428