

Short Communication

The Effect of Different Supports on the Characteristic and Catalytic Properties of Ni-Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/S (S= SiO₂ or Al₂O₃ or ASA) Nanocatalysts in Hydrocracking of *n*-decane

Hoda Amirmoghadam¹, Hamidreza Aghabozorg^{2,*}, Moayad Hossaini Sadr³,
Fathollah Salehirad² and Akbar Irandoukht²

¹Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran.

²Research Institute of Petroleum Industry, Tehran, Iran.

³Department of Chemistry, Azarbaijan Shahid Madani University, Tabriz, Iran.

(*)Corresponding author: aghabozorghr@ripi.ir

(Received: 27 January 2019 and Accepted: 16 September 2019)

Abstract

In this research, Ni-Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/S (S=SiO₂ or Al₂O₃ or ASA (amorphous silica alumina)) nanocatalysts with different supports were prepared via 2 steps with impregnation method and the effect of support on the characteristic and catalytic properties of the prepared samples was studied. The synthesized samples were characterized by X-ray diffraction (XRD), temperature programmed desorption (TPD), temperature programmed reduction (TPR), and energy dispersive X-ray spectroscopy (EDX). Morphology of the samples was studied by field emission scanning electron microscope (FE-SEM) and the surface area, pore volume and pore size of the catalysts were determined by BET (Brunauer-Emmett-Teller) method. In the XRD patterns of the prepared catalysts, the H₃PW₁₂O₄₀ (HPW) phase was observed. The FE-SEM images showed that the synthesized particles were in nanoscale. The results of TPD studies indicated that moderate acidic sites of Al₂O₃ supported nanocatalyst was more than the others. The catalytic activity of the nanocatalysts in hydrocracking of *n*-decane indicated that Al₂O₃ supported nanocatalyst had the highest catalytic activity.

Keywords: Heteropoly acid, Nanocatalyst, Hydrocracking, Al₂O₃.

1. INTRODUCTION

Generally, hydrocracking supported catalysts are bifunctional, i.e. the acid sites which provide the cracking function and metal sites with a hydrogenation-dehydrogenation function. Hence, hydrocracking catalysts are composed of acidic supports such as SiO₂, Al₂O₃, ZrO₂, active carbon, modified zeolite, etc., active metals, (e.g. Mo, W) and promoters (e.g. Ni, Co) [1, 2].

Heteropoly acids (HPA) and their Cs salts have witnessed rapid growth in the last decade as solid acid catalysts [3]. Heteropoly acids with Keggin structure offer several advantages in terms of catalytic performance as well as strong

acid and redox sites. However, the main disadvantage is their very low surface area (<10 m² g⁻¹) and hence it becomes necessary to disperse HPA on supports that possess a larger surface area [4, 5].

One approach to obtain supported HPA catalysts is the direct impregnation of the support with a heteropoly acid solution followed by evaporation of the solvent. Several supports, such as silica gel, alumina and mesoporous silica, SBA-15 [6, 7, 8, 9] have been used to enhance the dispersion of HPA, thereby increasing the accessibility to their acid sites while lowering their solubility in polar media. In

addition, the supports as acid sites have an important role in catalytic behavior of these catalysts in hydrocracking of n-decane. Therefore, many reports have been presented about applying different supports for these catalysts in order to use in hydrocracking of n-decane. For example, preparation and application of Ni-C_sH_{3-x}._xPW₁₂O₄₀/Al₂O₃ catalysts in hydrocracking of n-decane has been reported by Jin and co-worker [7]. In another work, the behavior of Ni-C_sH_{3-x}._xPW₁₂O₄₀/SiO₂ catalysts for hydrocracking of n-decane has been reported [4]. The hydrocracking of n-decane was carried out on a sulfided Ni-W/silica-alumina catalyst and for comparison on a sulfided Ni-W/USHY zeolite catalyst [19]. Since the comparison of these supports had not been reported, in this work we have used different supports and HPW for preparing new catalysts in order to study the effect of different support on the catalytic activity of Ni-Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/S (S=SiO₂ or Al₂O₃ or ASA). Hence, Ni-Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/S (S=SiO₂ or Al₂O₃ or ASA) nanocatalysts have been prepared by impregnation technique and characterized with conventional methods. The effect of different supports on the catalytic activity of the nanocatalysts has been studied in hydrocracking of n-decane.

2. EXPERIMENTAL

2.1. Materials and Method

The samples were prepared by using of impregnation method via 2 steps. First, the silica (Merck, specific surface area 697 m²g⁻¹, 40-70 mesh) or alumina (Sasol Chemical Co., specific surface area 273 m²g⁻¹, 40-70 mesh) or ASA support (Ripi., specific surface area 162 m²g⁻¹, 40-70 mesh) was impregnated with a solution containing the desired quantities of Ni(NO₃)₂ (BDH, 98%), (NH₄)₆Mo₇O₂₄.4H₂O (Merck, 99%), and Cs₂CO₃ (Merck, 99.99%). Impregnated samples were dried overnight at 120 °C and then calcined at 400 °C for 3 h using a heating ramp of 2 °Cmin⁻¹. In the second step, the obtained samples were

impregnated with a solution containing the desired quantities of H₃PW₁₂O₄₀ (Merck, 99%). The obtained products were finally dried overnight at 120 °C without calcination.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were obtained on X' Pert Pro diffractometer equipped with a copper anode (CuK α monochromatized radiation source ($\lambda=1.54056$ Å), $2\theta=10-80^\circ$).

Morphology and elemental analysis of the samples were studied by a field emission scanning electron microscope (FE-SEM) of TESCAN Mira3-XMU equipped with EDX (Energy dispersive X-ray spectroscopy) instrument. Surface area, pore size and pore volume of the catalysts were measured by Brunauer-Emmett-Teller (BET) method using N₂ on adsorption instrument (Quantasorb, Quantachrome). Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) studies were performed using a semiautomatic micrometrics TPD/TPR 2900 apparatus to investigate the reduction behavior and acid properties of the catalysts, respectively.

2.3. Catalytic Activity Evaluation

Catalytic performance of the prepared catalyst was evaluated in a 300 ml batch type stainless steel autoclave reactor (452 HC reactor, Parr instrument). The applied feed was n-decane (Merck, 99%). The reaction condition was as follow: 3.0 MPa, catalyst/n-decane weight ratio: 2/20, 300 °C and 4 h. Schematic diagram of the experimental setup for hydrocracking of n-decane is shown in Figure 1.

The reactants and products were analyzed by a gas chromatograph (VARIAN model CP-3800) equipped with capillary column (100 m) and FID detector. For comparison, a commercial hydrocracking catalyst (NiMo/ASA) was applied for hydrocracking of n-decane under the same condition. Conversion of the hydrocracking process was calculated

by Eq. 1 and selectivity of the catalyst to the desired product was obtained by Eq. 2.

$$\text{Conversion}\% = \frac{\sum X_i}{n_{\text{Feed}}} \times 100 \quad (1)$$

$$\text{Pi Selectivity}\% = \frac{X_i}{\sum X_i} \times 100 \quad (2)$$

Here P_i is a desired product and X_i is mole number of P_i and n_{Feed} is mole number of the feed.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Prepared Samples

The XRD patterns of Ni-Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/S (S=SiO₂ or Al₂O₃ or ASA) catalysts are presented in Figure

1. The comparison of the XRD patterns of the prepared catalysts indicates that the keggin structure of Cs_xH_{3-x}PW (JCPDS No: 50-1857) [10, 11] is observed in the patterns. The crystallite sizes of the prepared samples calculated by Scherrer equation using the intense peak ($2\theta = 26$) are presented in Table 1. This table shows that the size of the prepared particles is in nanoscale. By changing the support, there is a slight change in the crystallite sizes of the prepared samples. For example, crystallite size of synthesized sample with silica support was slightly larger than other samples.

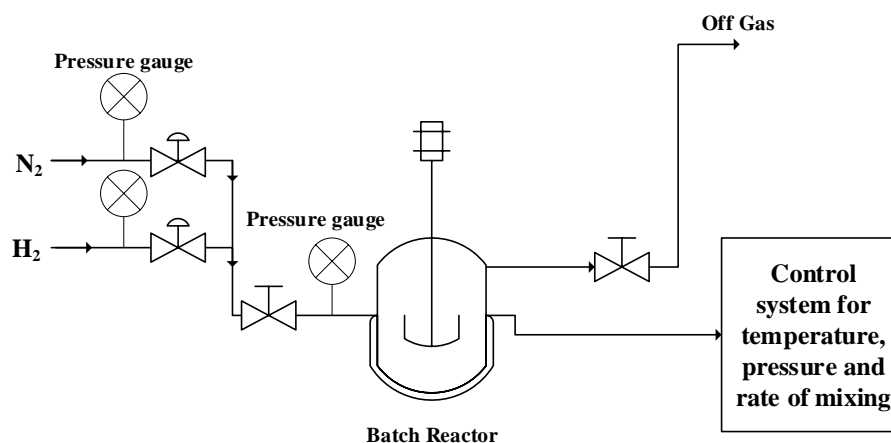


Figure 1. Schematic diagram of the experimental setup for hydrocracking of *n*-decane in 300 ml batch type stainless steel autoclave reactor.

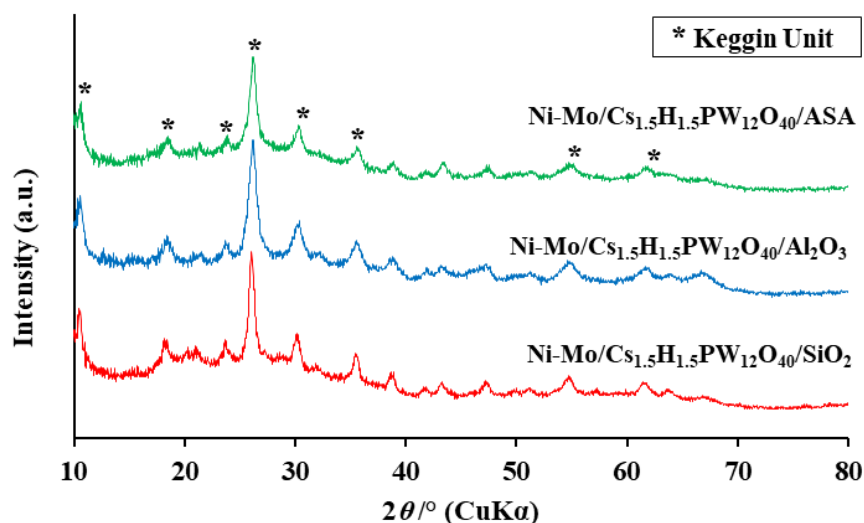


Figure 2. XRD patterns of the prepared samples.

3.2. Morphology of the Prepared Samples

The surface area, pore volume, pore size and elemental analysis of the catalysts are

given in Table 1. According to Table 1, surface area, pore volume, pore size of supports after impregnation decrease

remarkably. It is reported that during impregnation the pore walls of the support can be eroded with acidic HPW aqueous solution and also the pores partially can be blocked with nickel and molybdenum species which lead to reducing the surface area and pore volume of the supports [7, 12, 13]. In addition, according to the obtained results in Table 1, the surface area of Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/SiO₂ catalyst is more than the other samples while pore volume

of Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/Al₂O₃ is more than the others. Also, the pore size of the synthesized nanocatalysts is in the range of 3.5 to 7.3 nanometers that means all the samples are mesopore compounds.

The FE-SEM images of the prepared catalysts are indicated in Figure 3. These images show that the synthesized particles are actually agglomerated and homogenous nano-size crystallites are nearly in spherical shape.

Table 1. Elemental analysis results, crystallite size of the keggin structure of Cs_{1.5}H_{1.5}PW₁₂O₄₀ phase (Calculated by Scherrer equation) and Physical properties of the catalysts.

Samples	Element* (Wt%)					Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Crystallite size (nm)
	Cs	Ni	Mo	P	W				
SiO ₂	-	-	-	-	-	697	0.630	3.6	-
Al ₂ O ₃	-	-	-	-	-	273	0.718	10.5	-
ASA	-	-	-	-	-	163	0.540	13.1	-
Ni-Mo/Cs _{1.5} H _{1.5} PW ₁₂ O ₄₀ /SiO ₂	4.07	2.50	2.14	0.48	35.21	284	0.248	3.5	14.9
Ni-Mo/Cs _{1.5} H _{1.5} PW ₁₂ O ₄₀ /Al ₂ O ₃	4.30	2.32	2.20	0.78	34.20	162	0.298	7.3	9.7
Ni-Mo/Cs _{1.5} H _{1.5} PW ₁₂ O ₄₀ /ASA	4.02	2.80	2.96	0.66	33.53	100	0.157	6.2	11.9

*Calculated by EDX method

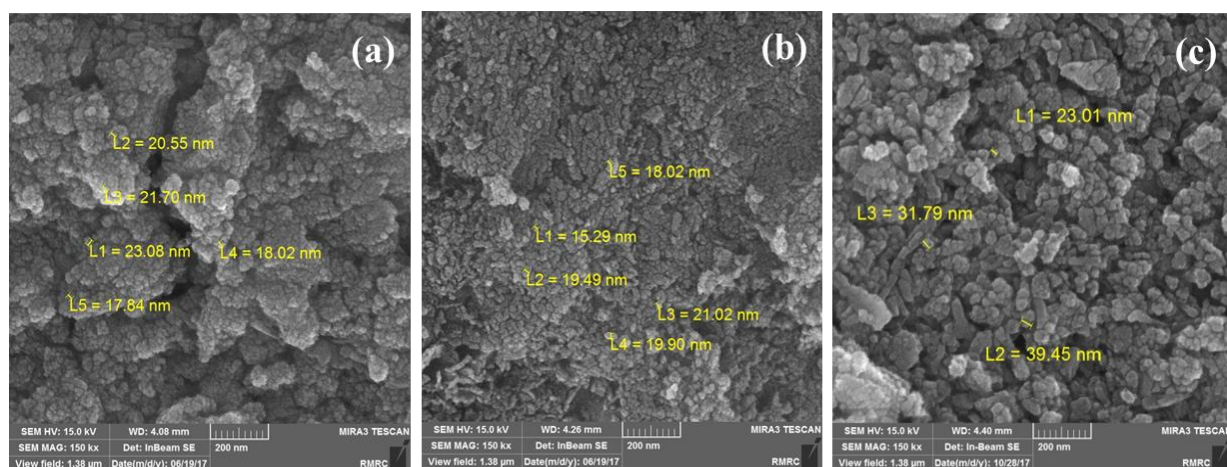


Figure 3. FE-SEM images of the prepared samples: (a) Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/SiO₂, (b) Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/Al₂O₃, and (c) Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/ASA.

3.3. TPD Profile of the Prepared Samples

The NH₃-TPD profiles of the prepared samples are shown in Figure 4. To compare the acidity distribution among the catalysts, the weak, medium, and strong acidities are assigned to the peak areas of NH₃-TPD curves below 350 °C, at 350–500 °C, and above 500 °C, respectively [14]. All profiles presented an intense peak

which can be assigned to weak acidic sites (150–350 °C). In addition, these profiles indicate that the moderate and strong acidic sites are remarkable in the Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/Al₂O₃ and Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/ASA samples. Mastikhin et al. proposed that the interaction between HPW and the surface of SiO₂ would reduce the acid strength [15]. These

results also show that total acid sites of Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/ASA sample (1,8143 mmole NH₃/g) is more than Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/SiO₂ and Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/Al₂O₃ samples while, the moderate acidic site of Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/Al₂O₃ catalyst is more than the others. These results also confirm that total acid sites of Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/ASA catalyst is more than the others (Table 2).

3.4. TPR Profile of the Prepared Samples

The H₂-TPR profiles of catalysts are shown in Figure 5. The differences observed in these profiles are due to the interactions between metals and support in each sample. In other words, when metals species are deposited on the support by impregnation, metal atoms interact with support OH groups and a new bond is formed between the metal and the support O atoms. This interaction is different for

the applied supports. Thus, metals are reduced at different temperatures [16]. The reduction of Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/SiO₂ nanocatalyst in the temperature range from 400 °C to 700 °C is decreased with respect to the other nanocatalysts. As it was said, this is due to the interaction of OH groups in the silica support with heteropoly acid protons. Also, the formation of strong bonds between different species of nickel and molybdenum together and interaction of these species with the support leads to the formation of complex compounds (for example, nickel silicate and nickel Molybdate [17]). For the synthesized nanocatalyst with alumina support, the peaks appeared to be more intense than other samples. It can be noticed from Table 2 that the H₂ consumption per gram of catalyst in Ni–Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/Al₂O₃ catalyst is higher than that of for the other samples that indicate higher reducibility of catalyst.

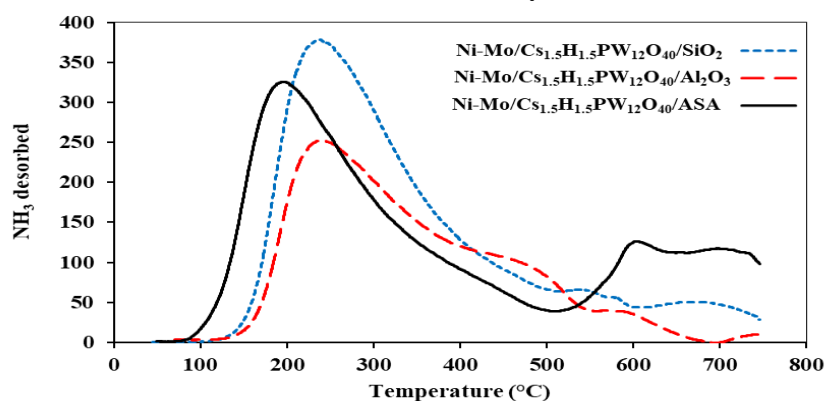


Figure 4. TPD profiles of the prepared nanocatalysts.

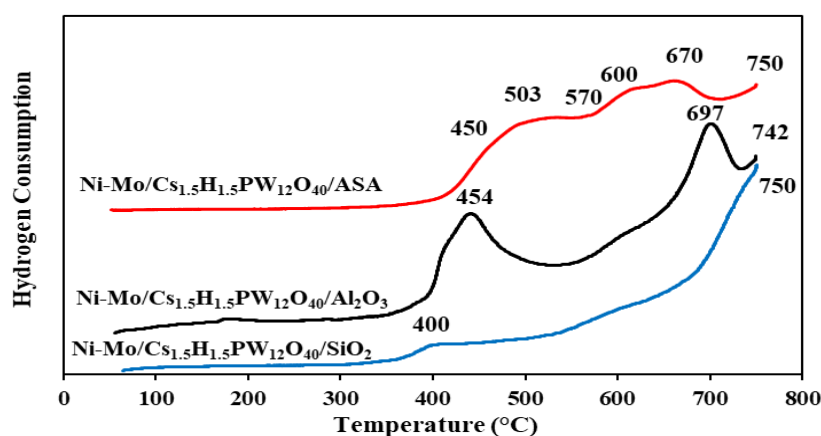


Figure 5. TPR profiles of the prepared nanocatalysts.

Table 2. H_2 and NH_3 consumption (mmol/g) of the prepared nanocatalysts.

Samples	H_2 consumption (mmol of H_2 /g cat)	NH_3 consumption (mmol of NH_3 /g cat)			
		weak	moderate	strong	total
$Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$	2.4307	1.4354	-	-	1.4354
$Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/Al_2O_3$	3.9023*	0.8754*	0.3441*	-	1.1295*
$Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/ASA$	2.6505	1.2833	-	0.5309	1.8143

*Obtained from [18]

3.5. Catalytic Activity

The catalytic evaluation results for the reduced $Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/S$ ($S=SiO_2$ or Al_2O_3 or ASA) nanocatalysts in hydrocracking of n-decane are shown in Figure 6 and Table 3. Classically, the middle acidity amount of a catalyst would favor the hydrocracking activity [4]. Hence, in the $Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/Al_2O_3$ catalyst, moderate acidic sites (0.3441 mmole NH_3/g) and total conversion (49.24%) are more than the other catalysts. Meanwhile, the activities of the prepared catalysts are more than the activity of commercial catalyst ($NiMo/ASA$). Furthermore, the order of the moderate acidity of the catalysts is coincident with the order of catalytic activity. It can be

concluded that more moderate acidity leads to more catalytic activity.

The distribution of the obtained products in the presence of the prepared catalysts for hydrocracking of n-decane is shown in Figure 6. For all the prepared catalysts the main products is C_6 hydrocarbons while the commercial catalyst leads to production of heavier hydrocarbon such as C_{10} hydrocarbons. Production of C_{10} hydrocarbons including 3-methyl nonane, 2-3-dimethyl octane and 3-3-4 trimethyl heptane. In addition, 94% of the C_6 components are branched hydrocarbons which confirm the isomerization process. Also, for all the samples the amounts of lighter hydrocarbons ($< C_4$) are negligible and selectivity of the catalysts for these compounds are not considered in Figure 6.

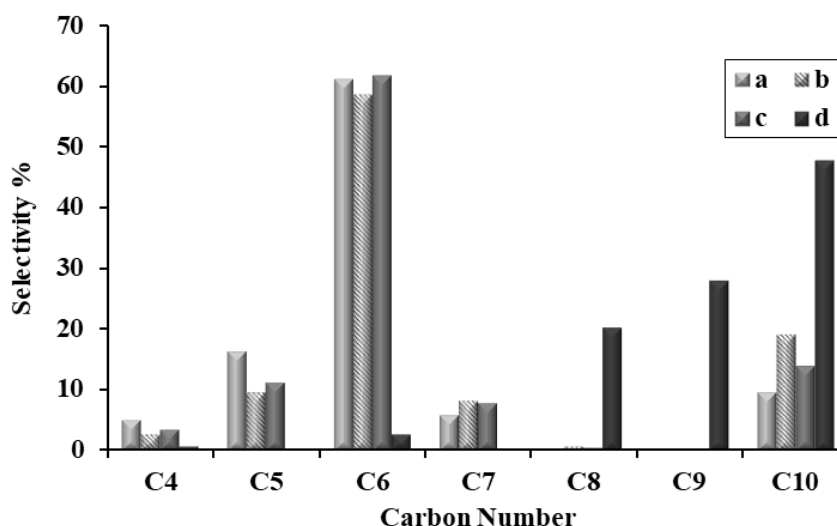


Figure 6. Selectivity of catalysts in hydrocracking of n-decane: (Reaction conditions: $T = 300^\circ C$, $P = 3$ Mpa, $t = 4$ h, 20g of n-decane and 2 g of the catalyst) (a) $Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$, (b) $Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/Al_2O_3$, (c) $Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/ASA$ and (d) Commercial catalyst

Table 3. Selectivity of prepared nanocatalysts in hydrocracking of n-decane and conversion of the nanocatalysts

Samples	Selectivity (%)							Conversion (%)
	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	
Ni-Mo/Cs _{1.5} H _{1.5} PW ₁₂ O ₄₀ /SiO ₂	5.1	16.4	61.7	6.0	0	0	9.6	32.15
Ni-Mo/Cs _{1.5} H _{1.5} PW ₁₂ O ₄₀ /Al ₂ O ₃	2.8	9.7	58.6	8.4	0.9	0	19.4	49.24
Ni-Mo/Cs _{1.5} H _{1.5} PW ₁₂ O ₄₀ /ASA	3.6	11.4	61.6	8.1	0.6	0	14.0	41.87
Commercial catalyst	0.7	0	2.8	0	20.5	28.2	47.8	25.55

4. CONCLUSION

In all the prepared nanocatalysts, the H₃PW₁₂O₄₀ (HPW) phase was observed. The FE-SEM images showed that the synthesized particles were in nanoscale. The NH₃-TPD results indicate that in Ni-Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/Al₂O₃ catalyst, moderate acidic sites are more than the other catalysts that has led to high activity. The nanocatalysts prepared with various support (silica, alumina and silica-alumina) were used as catalysts for hydrocracking of n-decane. The obtained results indicate that using different supports in these catalysts has an important role in chemical and physical properties and catalytic behavior of them in n-decane hydrocracking.

For all the prepared catalysts the main products is C₆ hydrocarbons while the commercial catalyst leads to production of heavier hydrocarbon such as C₁₀ hydrocarbons. The best result was obtained on the Ni-Mo/Cs_{1.5}H_{1.5}PW₁₂O₄₀/Al₂O₃ catalyst with n-decane conversion of 49.24%. The results show that C₆ and C₁₀ component are branched hydrocarbons which confirm the isomerization process is also occurred during hydrocracking process.

ACKNOWLEDGMENT

The authors are very thankful to Research Institute of Petroleum Industry (RIPI).

REFERENCES

- Cui, Q., Zhou, Y., Wei, Q., Yu, G., Zhu, L., (2013). "Performance of Zr- and P-modified USY-based catalyst in hydrocracking of vacuum gas oil", *Fuel Processing Technology*, 106: 439-446.
- Looi, P. Y., Mohamed, A. R., Tye, C. T., (2012). "Hydrocracking of residual oil using molybdenum supported over mesoporous alumina as a catalyst", *Chemical Engineering Journal*, 181–182: 717-724.
- Eom, H. J., Lee, D. W., Kim, S., Chung, S. H., Hur, Y. G., Lee, K. Y., (2014). "Hydrocracking of extra-heavy oil using Cs-exchanged phosphotungstic acid (Cs_xH_{3-x}PW₁₂O₄₀, x = 1-3) catalysts", *Fuel*, 126: 263–270.
- Jin, H., Guo, D., Sun, X., Sun, S., Liu, J., Zhu, H., Yang, G., Yi, X., Fang, W., (2013). "Direct synthesis, characterization and catalytic performance of non-sulfided Ni–Cs_xH_{3-x}PW₁₂O₄₀/SiO₂ catalysts for hydrocracking of n-decane", *Fuel*, 112: 134-139.
- Liu, L., Wang, B., Yonghua, D., Borgna, A., (2015). "Supported H₄SiW₁₂O₄₀/Al₂O₃ solid acid catalysts for dehydration of glycerol to acrolein: Evolution of catalyst structure and performance with calcination temperature", *Applied Catalysis A: General*, 489: 32-41.
- Frattini, L., Mark, I., Christopher, M. A., Wilson, K., Kyriakou, G., Lee, A. F., (2017). "Support enhanced α -pinene isomerization over HPW/SBA-15" *Applied Catalysis B: Environmental*, 200: 10–18.
- Jin, H., Yi, X., Sun, S., Liu, J., Yang, G., Zhu, H., Fang, W., (2012). "Hydrocracking of n-decane over non-sulfided Ni–Cs_xH_{3-x}PW₁₂O₄₀/Al₂O₃ catalysts", *Fuel Processing Technology*, 97: 52-59.
- De Mattos, F. C. G., De Carvalho, E. N. C. B., Freitas, E. F., De Paiva, M. F., Ghesti, G. F., De Macedo, J. L., Dias, S. C. L., Dias, J. A., (2017). "Acidity and Characterization of 12-Tungstophosphoric Acid Supported on Silica-Alumina", *J. Braz. Chem. Soc.*, 28: 336-347.
- Qiu, B., Yi, X. D., Lin, L., Fang, W.P., Wan, H.L., (2008). "The hydrocracking of n-decane over bifunctional Ni-H₃PW₁₂O₄₀/SiO₂ catalysts", *Catalysis Today*, 131: 464-471.
- Corma, A., Martinez, A., Martinez, C., (1996). "Acidic Cs⁺, NH₄⁺, and K⁺ Salts of 12-Tungstophosphoric Acid as Solid Catalysts for Isobutane/2-butene Alkylatio", *Journal of Catalysis*, 164: 422-432.

11. Narasimharao, K., Brown, D. R., Lee, A. F., Newman, A.D., Siril, P. F., Avenier, S. J., (2007). "Structure–activity relations in Cs-doped heteropolyacid catalysts for biodiesel production", *Journal of Catalysis*, 248: 226-234.
12. Ameen, M., Azizan, M. T, Ramli, A., Yusup, S., Yasir, M., (2016). "Physicochemical properties of Ni-Mo/ γ -Al₂O₃ catalysts synthesized via sonochemical method", *Procedia Engineering*, 148: 64-71.
13. Liu, H. P, Lu, G. Z., Guo, Y., Wang, Y.Q., Guo, Y. L., (2009). "Synthesis of mesoporous Pt/Al₂O₃ catalysts with high catalytic performance for hydrogenation of acetophenone", *Catalysis Communications*, 10: 1324-1329.
14. Jiang, J., Dong, Z., Chen, H., Sun, J., Yang, Ch., Cao, F., (2013). "The Effect of Additional Zeolites in Amorphous Silica–Alumina Supports on Hydrocracking of Semirefined Paraffinic Wax". *Energy and Fuels*, 27: 1035-1042.
15. Mastikhin, V. M., Kulikov, S. M., Nosov, A. V., Kozhevnikov, I. V., Mudrakovsky, I. L., Timofeeva, M. N., (1990). "¹H and ³¹P MAS NMR studies of solid heteropolyacids and H₃PW₁₂O₄₀ supported on SiO₂", *Journal of Molecular Catalysis*, 60: 65–70.
16. Maity, S. K., Ancheyta, J., Alonso Mohan, F., Rana, S., (2004). "Preparation, characterization and evaluation of Maya crude hydroprocessing catalysts", *catalysis Today*, 98: 193-199.
17. Reina, T. R., Yeletsky, P., Bermúdez, J. M., Arcelus-Arrillaga, P., Yakovlev, V. A., Millan, M., (2016). "Anthracene aquacacking using NiMo/SiO₂ catalysts in supercritical water conditions", *Fuel*, 182: 740–748.
18. Amimoghadam, H., Hossaini Sadr, M., Aghabozorg, H.R., Salehirad, F., Irandoukht, A., (2018). "The effect of molybdenum on the characteristics and catalytic properties of M/Cs_{1.5}H_{1.5}PW₁₂O₄₀/Al₂O₃ (M = Ni or/and Mo) nanocatalysts in the hydrocracking of n-decane", *Reaction Kinetics, Mechanisms and Catalysis*, 125: 983–994.
19. Roussel, M., Lemberon, J., Guisnet, M., Cseri, T., Benazzi, E., (2003). "Mechanisms of n-decane hydrocracking on a sulfided NiW on silica-alumina catalyst", *Journal of Catalysis*, 218: 427-437.