## **Short Communication**

# The Effect of Different Supports on the Characteristic and Catalytic Properties of Ni-Mo/Cs<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub>/S (S= SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> or ASA) Nanocatalysts in Hydrocracking of *n*-decane

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#### Abstract

In this research, Ni-Mo/Cs<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub>/S (S=SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> 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  $H_3PW_{12}O_{40}$  (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  $Al_2O_3$  supported nanocatalyst was more than the others. The catalytic activity of the nanocatalysts in hydrocracking of n-decane indicated that  $Al_2O_3$ supported nanocatalyst had the highest catalytic activity.

Keywords: Heteropoly acid, Nanocatalyst, Hydrocracking, Al<sub>2</sub>O<sub>3</sub>.

#### **1. INRODUCTION**

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 SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, 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  $(<10 \text{ m}^2 \text{ g}^{-1})$  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 ndecane. 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-Cs<sub>x</sub>H<sub>3</sub>-.xPW12O40/Al2O3 catalysts in hydrocracking of n-decane has been reported by Jin and co-worker [7]. In another work, the of behavior  $Ni-Cs_{x}H_{3-x}PW_{12}O_{40}/SiO_{2}$ 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- $Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/S$  (S=SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) or ASA). Hence, Ni-Mo/Cs<sub>15</sub>H<sub>15</sub>PW<sub>12</sub>O<sub>40</sub>/S (S=SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> or ASA) nanocatalysts prepared by impregnation have been and technique 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  $m^2g^{-1}$ , 40-70 mesh) or alumina (Sasol Chemical Co., specific surface area 273  $m^2g^{-1}$ , 40-70 mesh) or ASA support (Ripi., specific surface area 162  $m^2g^{-1}$ , 40-70 mesh) was impregnated with a solution containing the desired quantities of Ni(NO<sub>3</sub>)<sub>2</sub> (BDH, 98%), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O (Merck, 99%), and Cs<sub>2</sub>CO<sub>3</sub> (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<sup>-1</sup>. In the second step, the obtained samples were

impregnated with a solution containing the desired quantities of  $H_3PW_{12}O_{40}$  (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 $\alpha$  monochromatized radiation source ( $\lambda$ =1.54056 Å), 2 $\theta$ =10-80°).

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 Xray spectroscopy) instrument. Surface area, pore size and pore volume of the catalysts were measured by Brunauer-Emmett-Teller (BET) method using  $N_2$ 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.

reactants and The 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.

$$Conversion\% = \frac{\sum X_i}{n_{Feed}} \times 100 \tag{1}$$

$$Pi Selectivity\% = \frac{X_i}{\Sigma X_i} \times 100$$
(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<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub>/S (S=SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> 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<sub>x</sub>H<sub>3-x</sub>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 prepared samples. For example, the 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– $Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$  catalyst is more than the other samples while pore volume

of Ni–Mo/Cs<sub>1.5</sub> $H_{1.5}PW_{12}O_{40}/Al_2O_3$  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 homogenyeous nano-size crystallites are nearly in spherical shape.

**Table 1.** Elemental analysis results, crystallite size of the keggin structure of  $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ phase (Calculated by Scherrer equation) and Physical properties of the catalysts.

	Element* (Wt%)					Surface	Pore	Pore size	Crystallite
Samples	Cs	Ni	Мо	Р	W	area	volume	(nm)	size
						$(m^2g^{-1})$	(cm <sup>3</sup> g <sup>-1</sup> )		( <b>nm</b> )
SiO <sub>2</sub>	-	-	-	-	-	697	0.630	3.6	-
$Al_2O_3$	-	-	-	-	-	273	0.718	10.5	-
ASA	-	-	-	-	-	163	0.540	13.1	-
Ni-Mo/Cs <sub>1.5</sub> H <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub>	4.07	2.50	2.14	0.48	35.21	284	0.248	3.5	14.9
Ni-Mo/Cs <sub>1.5</sub> H <sub>1.5</sub> P W <sub>12</sub> O <sub>40</sub> /Al <sub>2</sub> O <sub>3</sub>	4.30	2.32	2.20	0.78	34.20	162	0.298	7.3	9.7
Ni-Mo/Cs <sub>1.5</sub> H <sub>1.5</sub> P W <sub>12</sub> O <sub>40</sub> /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)  $Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ , (b)  $Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/Al_2O_3$ , and (c)  $Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/ASA$ .

#### **3.3. TPD Profile of the Prepared Samples**

The NH<sub>3</sub>-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 NH<sub>3</sub>-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- $Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/Al_2O_3$ and Ni-Mo/Cs<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub>/ASA samples. Mastikhin et al. proposed that the interaction between HPW and the surface of SiO<sub>2</sub> would reduce the acid strength [15]. These results also show that total acid sites of Ni- $Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/ASA$  sample (1.8143) mmole  $NH_{3}/g$ ) is more than Ni– Mo/Cs1.5H1.5PW12O40/SiO2 Ni– and Mo/Cs<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub>/Al<sub>2</sub>O<sub>3</sub> samples while, moderate acidic site of Nithe Mo/Cs<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is more than the others. These results also confirm that total acid sites of Ni– Mo/Cs1.5H1.5PW12O40/ASA catalyst is more than the others (Table 2).

#### 3.4. TPR Profile of the Prepared Samples

The  $H_2$ -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<sub>15</sub>H<sub>15</sub>PW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> 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  $H_2$  consumption per gram of catalyst in Ni-Mo/Cs<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub>/Al<sub>2</sub>O<sub>3</sub> 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.

Samples	$H_2$ consumption	NH <sub>3</sub> consumption (mmol of NH <sub>3</sub> / g cat)					
	(initial of $H_2$ g cat)	weak	moderate	strong	total		
Ni-Mo/Cs <sub>1.5</sub> H <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub>	2.4307	1.4354	-	-	1.4354		
Ni-Mo/Cs <sub>1.5</sub> H <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub> /Al <sub>2</sub> O <sub>3</sub>	3.9023*	0.8754*	0.3441*	-	1.1295*		
Ni-Mo/Cs <sub>1.5</sub> H <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub> /ASA	2.6505	1.2833	-	0.5309	1.8143		

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

\*Obtained from [18]

#### 3.5. Catalytic Activity

The catalytic evaluation results for the Ni-Mo/Cs<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub>/S reduced (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, the  $Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/Al_2O_3$ in catalyst, moderate acidic sites (0.3441 total  $NH_3/g$ ) mmole and 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 = 4h, 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

Samplas		Selectivity (%)						
Samples	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	<b>C</b> <sub>7</sub>	C <sub>8</sub>	C9	C <sub>10</sub> 9.6 19.4 14.0 47.8	(%)
Ni-Mo/Cs <sub>1.5</sub> H <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub>	5.1	16.4	61.7	6.0	0	0	9.6	32.15
$Ni-Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/Al_2O_3$	2.8	9.7	58.6	8.4	0.9	0	19.4	49.24
<i>Ni-Mo/Cs</i> <sub>1.5</sub> <i>H</i> <sub>1.5</sub> <i>PW</i> <sub>12</sub> <i>O</i> <sub>40</sub> / <i>ASA</i>	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

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

#### **4. CONCLUSION**

In all the prepared nanocatalysts, the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (HPW) phase was observed. The FE-SEM images showed that the synthesized particles were in nanoscale. The NH<sub>3</sub>-TPD results indicate that in Ni- $Mo/Cs_{1.5}H_{1.5}PW_{12}O_{40}/Al_{2}O_{3}$ 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.

#### products is $C_6$ hydrocarbons while the commercial catalyst leads to production of hydrocarbon such heavier as $C_{10}$ hydrocarbons. The best result was obtained Ni-Mo/Cs<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub>/Al<sub>2</sub>O<sub>3</sub> on the catalyst with n-decane conversion of 49.24%. The results show that $C_6$ and $C_{10}$ component are branched hydrocarbons which confirm the isomerization process is also occurred during hydrocracking process.

For all the prepared catalysts the main

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