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Research Paper

## Investigation on bifunctional catalytic performance of (Pd+Pt)/HPW/UiO-66 for normal hexane hydroisomerization

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### 1. Abstract

One of the main objectives of refineries is to produce high-quality gasoline while respecting environmental standards. Accordingly, the normal hexane hydroisomerization and the preparation of appropriate catalysts for this process still pose a challenge in refineries. Therefore, in this work, heteropoly phosphotungstic acid (HPW), which contains high Brønsted acid sites, and the metal-organic framework UiO-66 were synthesized. Then, HPW/UiO-66 and (Pd+Pt)/HPW/UiO-66 samples were prepared by impregnation method to improve the stability of the catalyst. Finally, by adding platinum and palladium nanoparticles as promoters, the progress of the performance and activity of the catalyst in the normal hexane hydroisomerization was investigated. In addition, the characteristics of the synthesized samples were determined by XRD, FE-SEM, N<sub>2</sub> adsorption/desorption, and NH<sub>3</sub>-TPD analyses. Accordingly, in the presence of the bifunctional catalyst (0.2%Pd+0.3%Pt)/50%HPW/UiO-66, the selectivity of iso-hexane and the normal hexane conversion were obtained at 77.4 and 60%, respectively, after 36 h of reaction time.

**Keywords:** Hydroisomerization, Heteropoly Phosphotungstic Acid HPW, Metal-Organic Framework UiO-66, Promoter.

### 2. INTRODUCTION

The preparation of gasoline with a low olefin and aromatic content is a crucial challenge in refineries due to environmental regulations (Euro-4). The hydroisomerization of n-hexane increases research octane number (RON) and enhances gasoline quality. As a result, the octane number was set to 25 in the presence of n-hexane while being elevated to 74.5, 75.5, 94, and 105 by 2-methyl pentane, 3-methyl pentane, 2, 2-dimethyl butane, and 2, 3-dimethyl butane. The Hydroisomerization reaction is performed over a bifunctional catalyst that contains both Brønsted acid and metal sites [1,2]. Heteropolyacids are among the solid acid catalysts used in n-hexane hydroisomerization reactions, due to their high Brønsted acid sites. However, the small specific surface area, low porosity, and high solubility in polar solvents of heteropolyacids limit their application [3]. As a result, they must be supported by appropriate solids, such as metal-organic frameworks (MOFs), in order to achieve high specific surface areas and improve dispersion and stability. MOFs are highly porous materials with exceptional properties, such as controllable pore structures and extreme surface areas. UiO-66 with excellent chemical and thermal stability, and microporous structure is one of the Zr-based metal-organic framework materials [4]. In this study, the HPW, UiO-66, HPW/UiO-66, and (Pd+Pt)/HPW/UiO-66 catalysts, were synthesized and characterized by experimental techniques. Then the n-hexane hydroisomerization reaction was performed over these catalysts.

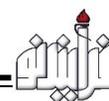
### 3. MATERIALS AND METHODS

A metal-organic framework UiO-66 was synthesized by hydrothermal reaction, and phosphotungstic acid (HPW) was synthesized by its precursor solution. Then HPW/UiO-66 and (Pd+Pt)/HPW/UiO-66 with different wt% were prepared by the impregnation method. Then, the characterization analysis (XRD, FE-SEM, N<sub>2</sub>adsorption/desorption, and NH<sub>3</sub>-

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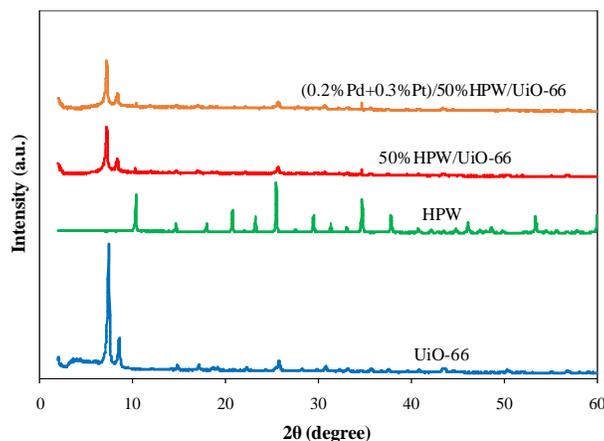
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TPD) was performed to verify that samples were correctly synthesized and to confirm that HPW and nanoparticles of Pd and Pt had been successfully impregnated into UiO-66.

#### 4. RESULTS AND DISCUSSION

The XRD patterns of synthesized samples are presented in Figure 1, confirming the formation of pure crystalline UiO-66 with the basic intensity peaks at  $2\theta$  of 7.3, 8.5, 25.5, and 30.6° [4]. The crystal planes (111) and (200) at  $2\theta$  of 7.3 and 8.5°, did not change by the impregnation of HPW and promoters. Besides, for the HPW sample, the characteristic peak at  $2\theta$  of 10.3°, 25.3° and 34.6° of high intensity was attributed to the Keggin structure [3]. XRD patterns of the synthesized samples were not significantly changed by the impregnation of nanoparticles of Pd and Pt, indicating high dispersion of these nanoparticles in the UiO-66 crystal structure.



**Figure 1.** XRD patterns of UiO-66, HPW, 50%HPW/UiO-66, and bifunctional catalyst (0.2%Pd+0.3%Pt)/50%HPW/UiO-66.

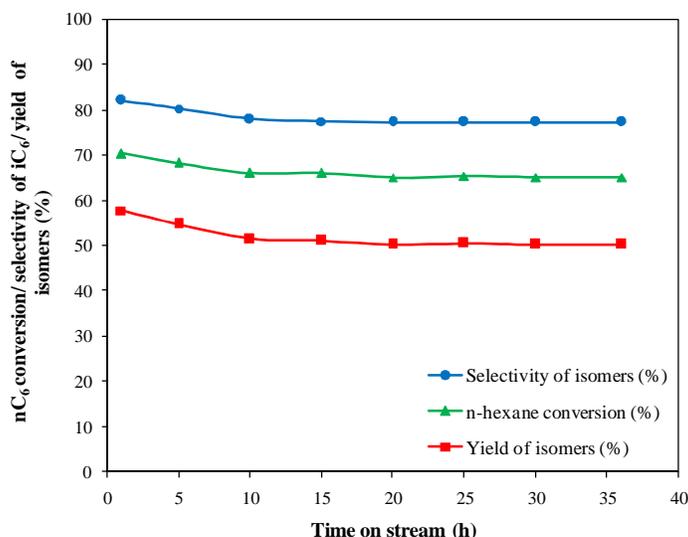
The n-hexane hydroisomerization process was carried out over synthesized samples in a fixed bed reactor in the laboratory-scale catalytic setup at 1 atm, and optimized operation conditions which were achieved in our previous work. Accordingly, the reaction was tested at 180 °C, WHSV of 3 h<sup>-1</sup>, and H<sub>2</sub>/nC<sub>6</sub> of 2 [5]. In order to improve the catalyst stability, HPW was impregnated into the UiO-66 structure. As a result, different weight percentages of HPW (10-60 wt%) were loaded to UiO-66 and tested in n-hexane hydroisomerization. According to the results, the 50%HPW/UiO-66 sample was the most active and the most selective compared to the other samples, with an iso-hexane selectivity of 61.3%, and n-hexane conversion of 58.4%. Finally, the bifunctional catalyst was prepared by impregnating the nanoparticles of Pd and Pt into the 50%HPW/UiO-66 structure to improve the catalytic performance. According to the results of Table 1, the bifunctional catalyst containing 0.2%Pd+0.3%Pt exhibited the best performance of n-hexane hydroisomerization reaction compared to the other samples. In addition, the bifunctional catalyst (0.2%Pd+0.3%Pt)/50%HPW/UiO-66 was examined over stability test for 36 h at 180 °C, WHSV of 3 h<sup>-1</sup>, and H<sub>2</sub>/nC<sub>6</sub> molar ratio of 2, as illustrated in Figure 2. As a result, there was no significant change in catalytic performance after 15 h of hydroisomerization reaction.

**Table 1.** The effect of nanoparticles of palladium and platinum in the activity improvement of the 50%HPW/UiO-66 catalyst in n-hexane hydroisomerization reaction at 180 °C, WHSV of 3 h<sup>-1</sup>, and H<sub>2</sub>/nC<sub>6</sub> of 2.

Bifunctional catalyst	0.5%Pd		0.4%Pd+0.1%Pt		0.3%Pd+0.2%Pt		0.2%Pd+0.3%Pt		0.1%Pd+0.4%Pt		0.5%Pt	
Reaction time (h)	1	15	1	15	1	15	1	15	1	15	1	15
nC <sub>6</sub> conversion (%)	62.4	60.1	64.5	62	66.4	63.1	70.3	66	71.2	67.4	72	69
Selectivity of iC <sub>6</sub> (%)	84	80.7	83.8	79.3	83.2	78	82.1	77.4	76.5	72.4	69	64
Yield (%)	52.4	48.5	54	49.2	55.2	49.2	57.7	51.1	54.4	48.8	49.7	44.1
C <sub>1</sub> -C <sub>5</sub> (%)	6.5	8.3	7.2	8.9	7.5	9.3	7.8	9.9	9.7	14.5	14.8	19.7
C <sub>7</sub> <sup>+</sup> hydrocarbon	6.3	9	5	8.9	5.3	9.7	6.2	9.7	9.4	10.4	10.9	13.5
Distribution of branched isomers (%)												
iC <sub>4</sub>	1.5	1	2	1.5	2.1	1.5	2.1	1.6	2.2	1.4	2.8	1.4
iC <sub>5</sub>	1.7	1	2	1.4	1.9	1.5	1.8	1.4	2	1.3	2.5	1.4



2,2-DMB	8.7	8.1	8.5	8	7.8	7.4	7.2	6.5	6.7	6	6.1	5.4
2,3-DMB	10.5	9.8	10.2	9.4	9.8	9	9.3	8.7	8.8	8.2	8.1	7.5
2-MP	27.4	27	27.7	27.2	31.4	28.5	32.1	30.3	30.2	29	26.3	24.7
3-MP	37.4	35.8	37.4	34.7	34.2	33.1	33.5	31.9	30.8	29.2	28.5	26.4



**Figure 2.** Investigation of the stability of the bifunctional catalyst (0.2%Pd+0.3%Pt)/50%HPW/UiO-66 in n-hexane hydroisomerization.

## 5. CONCLUSION

This study was conducted to describe the hydroisomerization reaction of n-hexane over the HPW/UiO-66 acid catalyst and improve the catalyst performance by adding platinum and palladium as promoters. According to the results, the bifunctional catalyst (0.2%Pd+0.3%Pt)/50%HPW/UiO-66 had a proper acidity of 0.851 mmol g<sup>-1</sup> with Brønsted acid sites and an appropriate specific surface area of 401.79 m<sup>2</sup> g<sup>-1</sup>. It showed an appropriate compromise between the iso-hexane selectivity and n-hexane conversion, achieving an iso-hexane selectivity of 77.4 %, a n-hexane conversion of 66%, and an iso-hexane production yield of 51.1% after 36 h of reaction time, at 180 °C, H<sub>2</sub>/nC<sub>6</sub> molar ratio of 2, and WHSV of 3 h<sup>-1</sup>.

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