Production of middle distillate through hydrocracking of paraffin wax over $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts: Effect of cesium content and surface acidity

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Abstract−Palladium-exchanged heteropolyacid ($Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$) catalysts were prepared by an ion-exchange method with a variation of cesium content (x=2.0, 2.2, 2.5, and 2.7) for use in the production of middle distillate through hydrocracking of paraffin wax. Surface acidity of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts determined by NH3-TPD experiments showed a volcano-shaped trend with respect to cesium content. Surface acidity of the catalysts played an important role in determining the catalytic performance in the hydrocracking of paraffin wax. Conversion of paraffin wax increased with increasing surface acidity of the catalyst, while yield for middle distillate showed a volcano-shaped curve with respect to surface acidity of the catalyst. Among the catalysts tested, $Pd_{0.15}Cs_{2.7}PW_{12}O_{40}$ catalyst with moderate surface acidity showed the best catalytic performance.

Key words: Hydrocracking, Middle Distillate, Paraffin Wax, Heteropolyacid, Surface Acidity

INTRODUCTION

Hydrocracking has been considered as a key process in petroleum refining for the production of fuels such as gasoline and middle distillate from heavy hydrocarbon [1-3]. Although crude oil has been traditionally used as a heavy hydrocarbon source, Fischer-Tropsch (FT) wax has many advantages over conventional crude oil in producing middle distillate through the hydrocracking process [4,5]. FT wax is typically composed of *n*-paraffins (>90%), alcohols, and olefins. Furthermore, FT wax is virtually free of sulfur (<5 ppm) and contains extremely low aromatic compounds (<1%). Therefore, middle distillate obtained from FT wax retains extremely low sulfur and aromatic contents, high cetane number, and clean burning feature in compression-ignition engines. For this reason, the production of middle distillate through hydrocracking of FT wax has been recognized as an economical and environmentally benign process.

Metal/acid bifunctional catalysts have been generally employed for hydrocracking process [6-10]. Alkanes are dehydrogenated on the metal sites and then isomerized or cracked on the acid sites through classical or non-classical carbenium ion chemistry [11-13]. Sulfide form of NiMo and NiW supported on alumina [14], silica-alumina [15], and molecular sieve [16] has been conventionally employed for the production of diesel-range hydrocarbon from crude oil. In the hydrocracking of FT wax (*n*-paraffin), however, noble metal catalysts supported on solid acid catalysts are known to be efficient, because these catalysts exhibit a high hydrogenation activity for hydrocracking of sulfur-free hydrocarbons [17,18].

Heteropolyacids (HPAs) are inorganic acids. It is known that acid strength of HPAs is stronger than that of conventional solid acids [19-21]. Most HPAs have low surface area (<10 m^2/g). However, insoluble HPA salts with K^+, Cs^+, and NH_4^+ cations have high surface area due to the formation of tertiary structure. In particular, HPA salts with Cs^+ cation ($Cs_xH_{3-x}PW_{12}O_{40}$) not only have high surface area (40-150 m^2/g) but also retain large surface acidity [22]. This implies that $Cs_xH_{3-x}PW_{12}O_{40}$ can serve as an efficient acid catalyst in the hydrocracking of paraffin wax.

In this work, palladium-exchanged HPA ($Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$) catalysts were prepared by an ion-exchange method with a variation of cesium content (x=2.0, 2.2, 2.5, and 2.7), and they were applied to the production of middle distillate through hydrocracking of paraffin wax. NH3-TPD experiments were conducted to measure the surface acidity of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts. The surface acidity of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts was then correlated with the catalytic performance in the hydrocracking of paraffin wax.

EXPERIMENTAL

1. Catalyst Preparation

$H_3PW_{12}O_{40}$ (Sigma-Aldrich) was thermally treated at 300 °C for 2 h for precise quantification, prior to the catalyst preparation. A set of palladium-exchanged HPA ($Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$) catalysts were prepared by an ion-exchange method with a variation of cesium content (x=2.0, 2.2, 2.5, and 2.7). A known amount of palladium nitrate ($Pd(NO_3)_2$, Sigma-Aldrich) and an appropriate amount of cesium nitrate ($CsNO_3$, Sigma-Aldrich) were separately dissolved in distilled water. These two solutions were then added dropwise into an aqueous solution of $H_3PW_{12}O_{40}$ with constant stirring. The resulting solution was slowly heated at 60 °C for 12 h to obtain a solid product. The solid product was dried overnight at 70 °C, and

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finally, it was calcined at 420 °C for 3 h to yield $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalyst. For comparison, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was also prepared by an ion-exchange method in the absence of palladium precursor.

2. Characterization

Surface area of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts was measured using a BET apparatus (Micromeritics, ASAP 2010). Crystalline phase of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts was investigated by XRD (Rigaku, D-MAX2500-PC) measurements. Successful formation of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ HPAs was confirmed by FT-IR (Nicolet, Impact 410) analyses.

Surface acidity of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts was measured by NH_3-TPD (temperature-programmed desorption) experiments. Each catalyst (0.2 g) was charged into a quartz reactor of the TPD apparatus (BELCAT-B, BEL Japan). The catalyst was pretreated at 200 °C for 1 h under a flow of helium (50 ml/min) to remove any physisorbed organic molecules. NH_3 (50 ml/min) was then introduced into the reactor at 50 °C for 30 min. Physisorbed NH_3 was removed at 150 °C for 1 h under flow of helium (50 ml/min). After the sample was cooled, the furnace temperature was increased from room temperature to 800 °C at a heating rate of 5 °C/min under a flow of helium (30 ml/min). The desorbed NH_3 was detected using a TCD (thermal conductivity detector) to measure total (surface and bulk) acidity. Bulk acidity of the catalyst was determined through calibration of experimentally measured bulk acidity of proton-form, by taking into account of the number of protons in the catalyst. Surface acidity was then calculated by subtracting bulk acidity from total (surface and bulk) acidity [19].

3. Hydrocrackig of Paraffin Wax

Hydrocracking of paraffin wax to produce middle distillate was carried out over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts in a stainless steel autoclave reactor (75 ml). 0.7 g of catalyst and 18 g of paraffin wax (Sigma-Aldrich) were charged into the reactor at room temperature. After being purged with nitrogen several times, the reactor was pressurized to 35 bar with hydrogen. The reactor was then heated to reaction temperature of 400 °C. A reaction was conducted for 2 h at hydrogen pressure of 60 bar. The products were analyzed using gas chromatographs (Younglin 600D and Younglin ACME 6100). For comparison and reference, the reaction was also conducted in the absence of catalyst. Carbon number distribution of paraffin wax reactant (melting point: 58-62 °C, ASTM D87) was in the range of C_{21}-C_{34}, as listed in Table 1. Wax conversion and product selectivity were calculated according to the Eqs. (1)-(4). Yield for middle distillate was calculated by multiplying conversion of wax and selectivity for middle distillate.

Wax (C_{21+}) conversion (%)

$$= \frac{\text{wt\% of } C_{21+} \text{ in the feed} - \text{wt\% of } C_{21+} \text{ in the product}}{\text{wt\% of } C_{21+} \text{ in the feed}} \times 100 \quad (1)$$

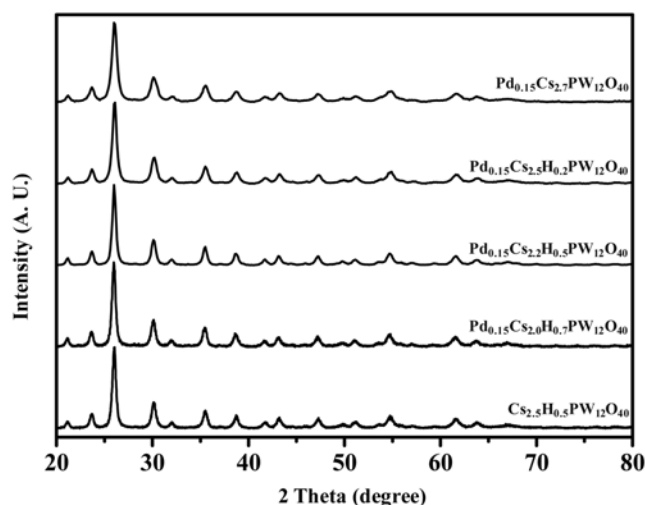C_1-C_4 selectivity (%)

$$= \frac{\text{wt\% of } C_1\text{-}C_4 \text{ in the product}}{\text{wt\% of } C_{21+} \text{ in the feed} - \text{wt\% of } C_{21+} \text{ in the product}} \times 100 \quad (2)$$

C_5-C_9 selectivity (%)

Table 2. BET surface area of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts

Catalyst	BET surface area (m^2/g)
$Pd_{0.15}Cs_{2.0}H_{0.7}PW_{12}O_{40}$	36
$Pd_{0.15}Cs_{2.2}H_{0.5}PW_{12}O_{40}$	39
$Pd_{0.15}Cs_{2.5}H_{0.2}PW_{12}O_{40}$	84
$Pd_{0.15}Cs_{2.7}PW_{12}O_{40}$	93

Fig. 1. XRD patterns of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts calcined at 420 °C.

$$= \frac{\text{wt\% of } C_5\text{-}C_9 \text{ in the product}}{\text{wt\% of } C_{21+} \text{ in the feed} - \text{wt\% of } C_{21+} \text{ in the product}} \times 100 \quad (3)$$

C_{10}-C_{20} (middle distillate) selectivity (%)

$$= \frac{\text{wt\% of } C_{10}\text{-}C_{20} \text{ in the product}}{\text{wt\% of } C_{21+} \text{ in the feed} - \text{wt\% of } C_{21+} \text{ in the product}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

1. Characterization

BET surface area of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts is summarized in Table 2. BET surface area of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts was much higher than that of $H_3PW_{12}O_{40}$ (6 m^2/g). This indicates that porous structure was developed in the $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts by forming a tertiary structure [23]. BET surface area of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts was increased with increasing cesium content, as reported in a previous work [24].

Successful formation of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts was well confirmed by XRD and FT-IR measurements. Fig. 1 shows the XRD patterns of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts calcined at 420 °C. No difference in XRD patterns was observed in all the catalysts, and only diffraction peaks corresponding to $Cs_xH_{3-x}PW_{12}O_{40}$ appeared in all the catalysts [25]. This indicates that $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts were successfully prepared. It should be noted that no peaks for Pd species were

Table 1. Carbon number distribution of paraffin wax

Carbon number	21	22	23	24	25	26	27	28	29	30	31	32	33	34
wt%	0.4	1.0	2.8	5.5	9.1	11.3	11.8	10.9	9.7	8.7	10.4	10.3	7.8	0.3
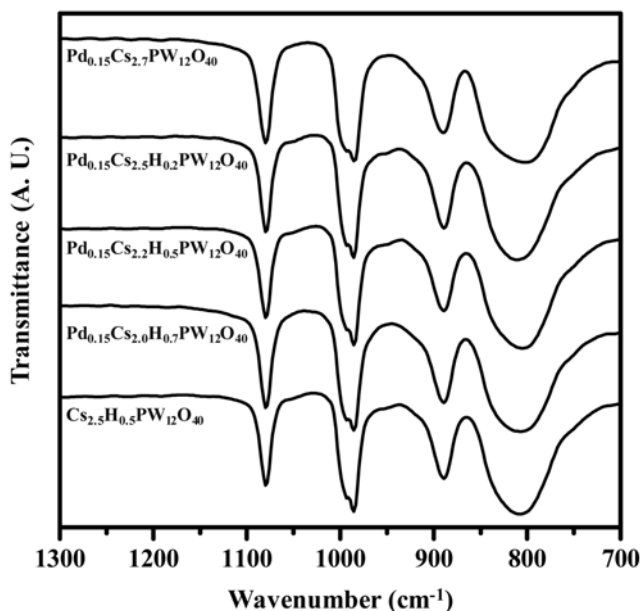
Fig. 2. FT-IR spectra of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalysts calcined at 420 °C.

Fig. 3. Carbon number distribution of paraffin wax (reactant) and product over Pd$_{0.15}$Cs$_{2.7}$PW$_{12}$O$_{40}$ catalyst.

found in the Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts, which indicates that Pd species were finely dispersed in the Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts.

Fig. 2 shows the FT-IR spectra of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalysts calcined at 420 °C. All the catalysts showed four characteristic IR bands of heteropolyanions in the range of 700-1,200 cm^{-1}, indicating that Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalysts were not thermally decomposed during the calcination at 420 °C [26]. The above result also supports that Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalysts were successfully prepared in this work.

2. Hydrocracking of Paraffin Wax over Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$

Catalytic performance of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalysts for hydrocracking of paraffin wax performed at 400 °C and 60 bar for 2 h is summarized in Table 3. In the absence of catalyst, conversion of wax and yield for middle distillate were very low, although selectivity for middle distillate was high. This result indicates that mild hydrocracking occurred in the absence of catalyst. Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalyst showed an enhanced conversion of wax compared to the case of no catalyst due to its large surface acidity.

Table 3. Catalytic performance of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalysts for hydrocracking of paraffin wax

Catalyst	C$_{21+}$ conversion	Product selectivity (%)			C$_{10}$-C$_{20}$ yield (%)
		C$_1$-C$_4$	C$_5$-C$_9$	C$_{10}$-C$_{20}$	
No catalyst	11.0	21.1	30.5	48.4	5.3
Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$	21.4	19.7	55.9	24.4	5.2
Pd$_{0.15}$Cs$_{2.0}$H$_{0.7}$PW$_{12}$O$_{40}$	38.1	13.8	57.5	28.7	10.9
Pd$_{0.15}$Cs$_{2.2}$H$_{0.5}$PW$_{12}$O$_{40}$	47.9	14.1	61.6	24.3	11.6
Pd$_{0.15}$Cs$_{2.5}$H$_{0.2}$PW$_{12}$O$_{40}$	61.2	19.7	59.4	20.9	12.8
Pd$_{0.15}$Cs$_{2.7}$PW$_{12}$O$_{40}$	58.8	15.9	60.2	23.9	14.1
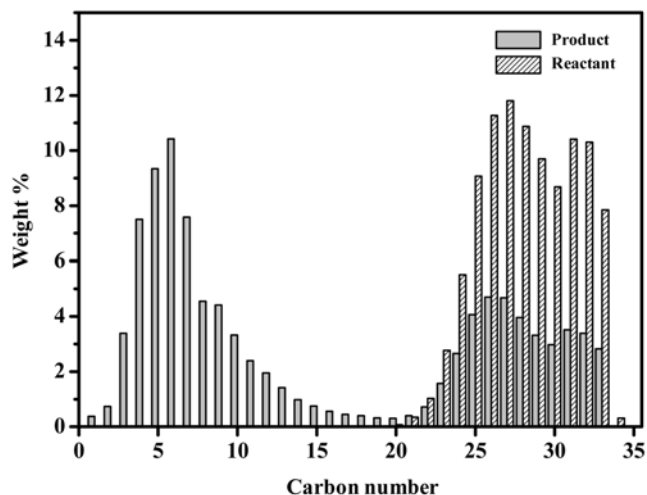
However, selectivity for middle distillate over Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalyst was very low. As a consequence, yield for middle distillate over Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalyst was almost identical to that obtained in the absence of catalyst.

It has been reported that Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalyst retains the highest surface acidity among Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$ catalysts (x=0-3) [27]. Therefore, Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ was chosen and tested as a reference. As listed in Table 3, however, Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts exhibited better catalytic performance than Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ catalyst in the hydrocracking of paraffin wax, in terms of conversion of wax and yield for middle distillate. It is believed that the enhanced catalytic performance of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts was attributed to the presence of palladium as a metal site, which was responsible for hydrogenation and dehydrogenation of hydrocarbon in the hydrocracking of paraffin wax over metal/acid bifunctional catalyst. This indicates that metal/acid bifunctional catalyst was more favorable than acid catalyst for the production of middle distillate through hydrocracking of paraffin wax. This result was well consistent with previous reports [6-10]. Among the catalysts tested, Pd$_{0.15}$Cs$_{2.7}$PW$_{12}$O$_{40}$ catalyst showed the highest yield for middle distillate.

Fig. 3 shows the carbon number distribution of paraffin wax (reactant) and product over Pd$_{0.15}$Cs$_{2.7}$PW$_{12}$O$_{40}$ catalyst. The result clearly shows that much portion of paraffin wax was hydrocracked to light hydrocarbons including middle distillate. This result also supports that Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts are suitable for the production of middle distillate through hydrocracking of paraffin wax.

3. Surface Acidity of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ Catalysts

NH$_3$-TPD experiments were carried out in order to determine the surface acidity of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts, and in turn, to elucidate the different catalytic performance of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts. Fig. 4 shows the NH$_3$-TPD profiles of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts. All the catalysts showed two desorption peaks. Total acidity of the catalysts decreased with increasing cesium content in the Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts.

It is generally accepted that non-polar molecules are adsorbed and react only on the surface of heteropolyacid catalyst, indicating that paraffin wax reacts on the surface of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ cata-
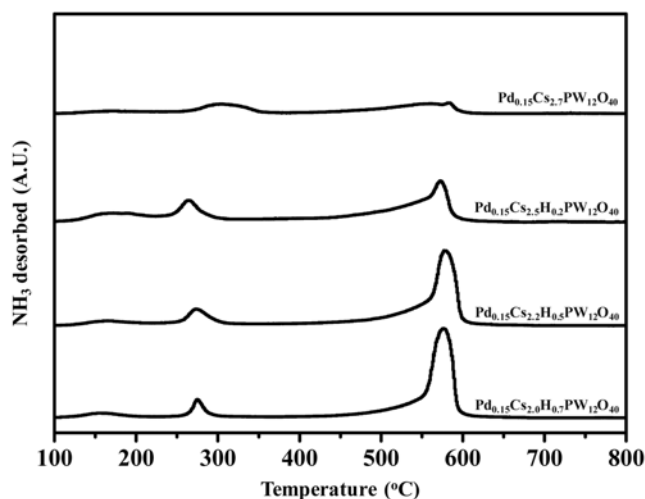
Fig. 4. NH₃-TPD profiles of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts.

Table 4. Surface acidity of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts

Catalyst	Surface acidity (μmol-NH₃/g)
Pd$_{0.15}$Cs$_{2.0}$H$_{0.7}$PW$_{12}$O$_{40}$	27.0
Pd$_{0.15}$Cs$_{2.2}$H$_{0.5}$PW$_{12}$O$_{40}$	29.7
Pd$_{0.15}$Cs$_{2.5}$H$_{0.2}$PW$_{12}$O$_{40}$	35.2
Pd$_{0.15}$Cs$_{2.7}$PW$_{12}$O$_{40}$	33.4

lysts in our hydrocracking reaction [19,28]. Therefore, it is believed that not total acidity but surface acidity of the catalyst may serve a crucial factor determining the catalytic performance in the hydrocracking of paraffin wax. Surface acidity of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts was determined by subtracting bulk acidity from total acidity of the catalysts. As listed in Table 4, surface acidity of the catalyst decreased in the order of Pd$_{0.15}$Cs$_{2.5}$H$_{0.2}$PW$_{12}$O$_{40}$>Pd$_{0.15}$Cs$_{2.7}$PW$_{12}$O$_{40}$> Pd$_{0.15}$Cs$_{2.2}$H$_{0.5}$PW$_{12}$O$_{40}$>Pd$_{0.15}$Cs$_{2.0}$H$_{0.7}$PW$_{12}$O$_{40}$.
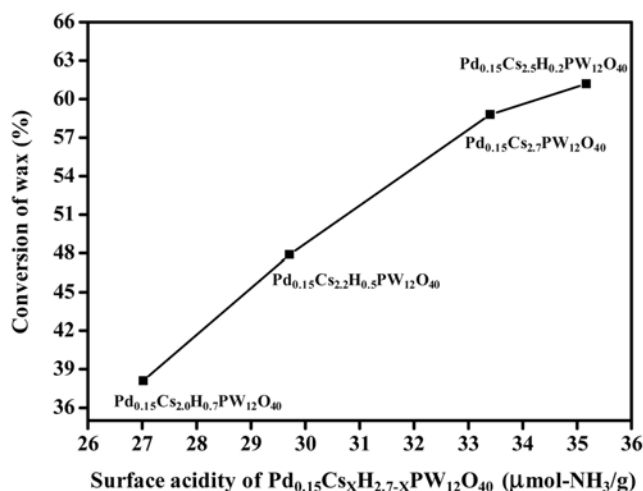
Fig. 5. Correlation between surface acidity and conversion of paraffin wax over Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts. Conversion of paraffin wax and surface acidity was taken from Tables 3 and 4, respectively.

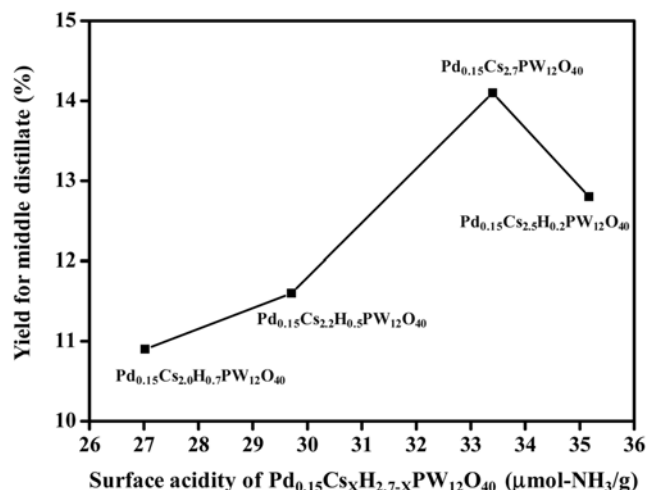**Fig. 6. Correlation between surface acidity and yield for middle distillate over Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts. Yield for middle distillate and surface acidity was taken from Tables 3 and 4, respectively.**

4. Correlation between Surface Acidity and Catalytic Performance

Fig. 5 shows the correlation between surface acidity and conversion of paraffin wax over Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts. Conversion of paraffin wax increased with increasing surface acidity of the catalyst. This can be understood by the fact that the hydrocracking ability of the catalyst increased with increasing acid property of the catalyst in the hydrocracking of paraffin wax.

Fig. 6 shows the correlation between surface acidity and yield for middle distillate over Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts. It is interesting to note that yield for middle distillate showed a volcano-shaped curve with respect to surface acidity of the catalyst. This indicates that optimal surface acidity of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts was required for maximum production of middle distillate through hydrocracking of paraffin wax. It is believed small surface acidity of Pd$_{0.15}$Cs$_{2.0}$H$_{0.7}$PW$_{12}$O$_{40}$ catalyst led to low conversion of wax, and in turn, low yield for middle distillate. It can also be inferred that Pd$_{0.15}$Cs$_{2.5}$H$_{0.2}$PW$_{12}$O$_{40}$ catalyst caused deep hydrocracking of paraffin wax to form undesired light hydrocarbon product due to its large surface acidity. Among the catalysts tested, Pd$_{0.15}$Cs$_{2.7}$PW$_{12}$O$_{40}$ catalyst with moderate surface acidity showed the highest yield for middle distillate.

CONCLUSIONS

Palladium-exchanged heteropolyacid (Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$) catalysts were prepared by an ion-exchange method with a variation cesium content (x=2.0, 2.2, 2.5, and 2.7), and they were applied to the production of middle distillate through hydrocracking of paraffin wax. Successful formation of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts was confirmed by XRD and FT-IR measurements. NH₃-TPD experiments were conducted to determine the surface acidity of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts. Surface acidity of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts showed a volcano-shaped trend with respect to cesium content. It was revealed that surface acidity of the catalysts served as a crucial factor determining the catalytic performance of Pd$_{0.15}$Cs$_x$H$_{2.7-x}$PW$_{12}$O$_{40}$ catalysts in the hydrocracking of paraffin wax.

Conversion of paraffin wax increased with increasing surface acidity of the catalyst, while selectivity for middle distillate decreased with increasing surface acidity of the catalyst. As a consequence, yield for middle distillate showed a volcano-shaped curve with respect to surface acidity of the catalyst. Among the catalysts tested, $Pd_{0.15}Cs_{2.7}PW_{12}O_{40}$ retaining moderate surface acidity exhibited the highest yield for middle distillate. It is concluded that optimal surface acidity of $Pd_{0.15}Cs_xH_{2.7-x}PW_{12}O_{40}$ catalysts was required for maximum production of middle distillate through hydrocracking of paraffin wax.

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