선택적 흡착법을 이용한 FCC공정의 C4 유분 탈황

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Sulfur removal in FCC C4 by selective adsorption for ultra-clean fuels

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Introduction

As the dwindling an estimated amount of oil deposits, various refinery processes are running all over the world. Among this processes, the fluid catalytic cracking (FCC) process is one of the most important for economical efficiency and to satisfy the high regulations. In these days fact, various desulfurization processes are running to remove the sulfur compound in commercial fuels. Above all, hydrodesulfurization (HDS) processes have been employing to reduce sulfur levels from commercial fuels. However, the current HDS process is difficult in reducing sulfur level because of very low reactivity of HDS catalysts for sulfur compounds. It means that achieving deep desulfurization levels would require increasing existing reactor sizes and increasing hydrogen consumption. One way to avoid the increased costs is to use different approaches, such as adsorption, which operates at ambient condition. In the present study, non-impregnated activated carbon (NIAC), CuCl impregnated activated carbon (CuCl/AC) and $PdCl_2$ impregnated activated carbon ($PdCl_2$/AC) were prepared and examined to develop efficient adsorbent for FCC refinery process. Our goal is to reduce this organic sulfur compounds below 1ppmw of sulfur from FCC C4 in order to prepare refined source of clean fuels. The effect of the species of the metal halides impregnated on the adsorptive properties was studied using CuCl/AC and PdCl2/AC. The factors that affect the sulfur adsorption capacities are discussed on the basis of chemical and structural properties of metal halide impregnated activated carbon as adsorbents.

Experimental

Three type of activated carbon (AC) was used in this study to analyze the effect of the pore size distribution. Among the AC studied were K-1 (Kaya activated carbon inc.), H-1 (Hanil tech inc.) and PCB (Calgon corporation), respectively. To prepare the metal halide impregnated AC adsorbent, starting support material was PCB having well-developed microporosity. The CuCl/AC and $PdCl_2$/AC were prepared following the incipient wetness method. These samples were washed with de-ionized water and dried in vacuum condition at 130 ℃ for 12h. Before the adsorption experiment, all the samples were purged in situ in a sus-cloumn under ultra pure nitrogen and activated under helium condition at 130℃ for 3h. Bet specific surface area was measured by nitrogen adsorption at -196℃ using a micrometrics (asap-2400). x-ray fluorescence (XRF) analysis was alppied to obtain the amount of impregnated metal halide on adsorbents. Elemental analysis of the AC samples was performed using Flash EA 1112 Thermo Finnigan elemental analyzer. All the samples were analyzed in liquid phase using liquid sampling valve and HP 6890 series gas chromatograph, equipped

with SUPELCO GAS-PRO sulfur capillary column and flame photometric detector (FPD). The FCC C_4 was obtained from SK corporation located in UL-SAN, KOREA. To obtain the Langmuir and Freundlich isotherm and to predict the maximum sulfur adsorption capacity of the adsorbents, sulfur removal experiment was carried out in a stirred batch system at 25℃, 10atm that is the same condition with the FCC refinery process. All dynamic adsorption experiments or breakthrough tests were carried out in sus-column, having an 8mm of inside diameter and 12mm of outside diameter, with a column length of 250 mm. The adsorption amounts were obtained after the following equation.

$$q_{breakthough} = \left(\frac{v}{m_{adsorbent}} \right) \times \left(\frac{\rho_{fuel}}{MW_{sulfur}} \right) \int_0^t \left[\frac{C(t)}{C_i} \right] dt$$

Result & Discussion

To investigate the sulfur adsorption capacity of NIAC as a support material, adsorption equilibrium experiments were carried out using three type of activated carbons at 25℃, 10 atm that is the same condition with FCC refinery process. Structural properties of each sample were calculated by bet method. The structural properties and its sulfur adsorption capacities were shown in Table 1. To further investigate the role of AC as support material on sulfur removal, the correlations between the structural properties and sulfur adsorption capacity of AC were found. According to the result of Table 1, Adsorption capacity of adsorbents is strongly depended on the pore distribution of adsorbent. When insufficient pore width, adsorbates could not enter into the inside of the pore in adsorbent and have no chance to adsorb with adsorbent. In case of greatly larger than the pore width comparing with the diameter of adsorbates, it could be in and out, easily. Table 1 shows the adsorption capacities of type K-1, H-1 and C-1. The pore size distribution of each samples had strong influence on maximum sulfur adsorption capacity. Because of the diameters of MM and DMDS molecules are 0.42 and 0.53 nm, sulfur adsorption capacity was the most high in type C-1 and decreased as growing the difference with adequate pore distribution.

<Table 1> Structural parameters of AC calculated from nitrogen adsorption at 77K

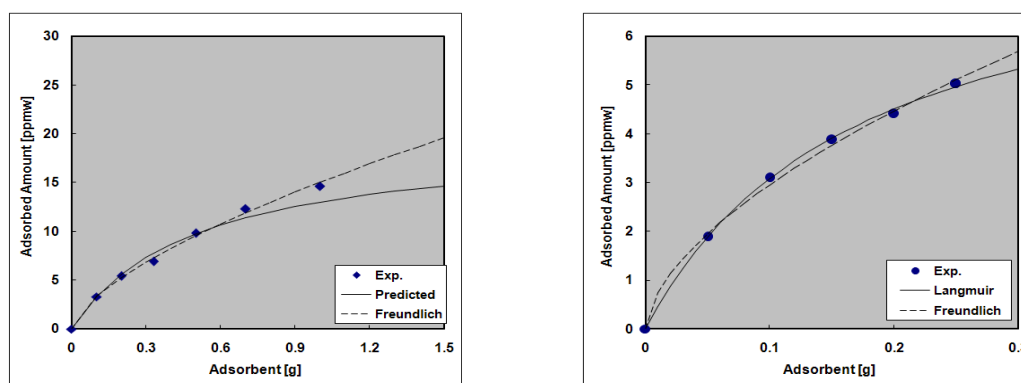| Sample	BET surface area (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{micro}/V_{total}	Sulfur adsorption capacity (wt% g^s/g_{ads})
K-1	1280	0.62	0.11	0.17	0.19
H-1	973	0.44	0.17	0.38	0.38
C-1	964	0.43	0.28	0.65	0.52

The NIAC, CuCl/AC (having CuCl content 2.5, 5.0, 7.5, and 10.0wt%) and PdCl2/AC (having $PdCl_2$ content 2.5, 5.0, 7.5, and 10.0wt%) were prepared by incipient wetness method to perform the adsorption equilibrium experiment and breakthrough experiment for developing the efficient adsorbent for FCC refinery process. The CuCl and PdCl2 contents of the adsorbents used in this study were analyzed by XRF. The content of CuCl in CuCl/AC clearly increases from 0.56 for NAC to 8.12% and the content of $PdCl_2$ of $PdCl_2$/AC increased to 8.12%. This

shows that CuCl and PdCl₂ particles were impregnated on the surface of the activated carbon, successfully. Table 2 shows the results of the elemental analysis of NIAC, 5wt% CuCl/AC and 5wt% PdCl₂/AC.

<Table 2> Elimental analysis of adsorbent samples

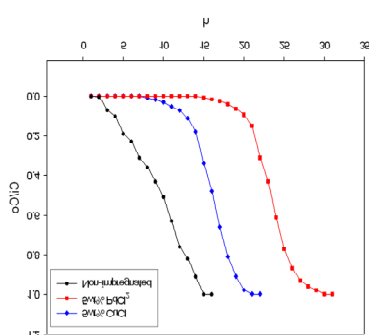| Sample	Elements (%)			
	C	H	N	Other
NIAC	80.35	2.37	0.43	16.41
5.0 wt% CuCl/AC	74.79	2.69	0.44	20.88
10.0 wt% CuCl/AC	72.91	2.76	0.43	22.10
5.0 wt% PdCl₂/AC	73.74	1.82	0.45	22.66
10.0 wt% PdCl₂/AC	70.04	2.03	0.43	25.87

In this study, the adsorption equilibrium experiments of sulfur compound in FCC C₄ were performed on the NIAC, 5.0wt% CuCl/AC and 5.0wt% PdCl₂/AC. Adsorption isotherm is essential for the description of how adsorbates will interact with impregnated AC is useful in optimizing the use of impregnated AC as adsorbent for sulfur removal. Adsorption isotherms for the CuCl/AC and PdCl₂/AC were illustrated in Figure 1, respectively. The obtained data at equilibrium were also fitted to Fruendlich and Langmuir isotherm models. Both adsorbents are well fitted the Freundlich isotherm considerably better than the Langmuir isotherm as the regression coefficient of the Freundlcih isotherm were 0.995 and 0.993 as compared to its Langmuir isotherm 0.983 and 0.954, respectively. Figure 1 showed that the adsorption capacity of PdCl₂/AC was greater than CuCl/AC.
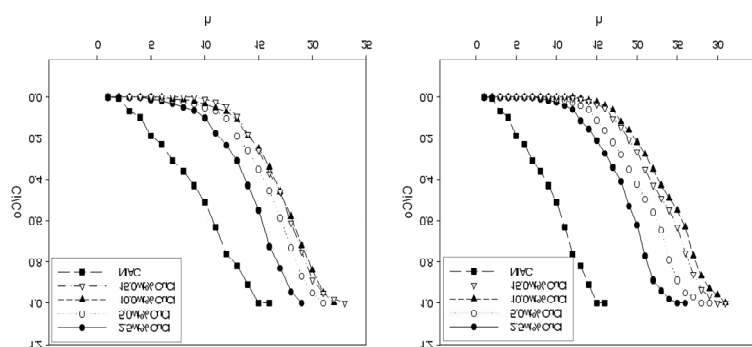

<Fig 1> Langmuir and Freundlich isotherm of CuCl/AC and PdCl₂/AC

Figure 2 shows that the breakthrough and saturation curves for total sulfur compound in FCC C₄ with three carbon-based adsorbents, NIAC, CuCl/AC and PdCl₂/AC. These adsorbents werecapable of removing 0.052wt% g^s/g_{ads}, 0.221wt% g^s/g_{ads} and 0.327wt% g^s/g_{ads} of sulfur adsorption capacity per gram of saturation time. Compared to NIAC, metal halide impregnated activated carbon shows significantly high sulfur adsorption capacities from the result of breakthrough curves. It is obvious evidence that impregnation of metal halide can improve the sulfur adsorption capacity via the interaction between the sulfur compound and adsorbent.

Figure 2 also shows the difference of sulfur adsorption capacity between CuCl/AC and PdCl$_2$/AC. The interactions between sulfur compound and adsorbent are strongly depended on the species of metal halide in the adsorbent. The adsorption capacities were 0.121 and 0.223wt% g^s/g$_{ads}$ for CuCl/AC, 0.221 and 0.327wt% g^s/g$_{ads}$ for PdCl$_2$/AC. In order to evaluate the performance of different content of metal halide impregnated activated carbon, CuCl/AC (having CuCl content 2.5, 5.0, 10.0, and 15.0wt%) and PdCl$_2$/AC (having PdCl$_2$ content 2.5, 5.0, 10.0, and 15.0wt%) were used for breakthrough experiments at the same condition with FCC process. Figure 3 shows that the breakthrough and saturation curves for the different content of CuCl/AC and PdCl$_2$/AC.

<Figure 2> Breakthrough experiment of NIAC, CuCl/AC and PdCl$_2$/AC

<Figure 3> Breakthrough experiment of different content of CuCl/AC and PdCl$_2$/AC

Conclusion

The sulfur adsorption capacity of AC as support material can be improved by developing narrow pore size distribution for each sulfur component. In this paper, C-1 is the most effective supported material for impregnation of metal halide. The CuCl/AC and PdCl$_2$/AC were successfully prepared by incipient wetness method as sulfur removal adsorbent for FCC refinery process. The experimental adsorption isotherms were compared with Langmuir and Freundlich models by the nonlinear least-squares estimate method. The Freundlich model gave the best fit with a correlation coefficient about 0.98, suggesting a surface adsorption mechanism on the prepare adsorbents. The NIAC, 10.0wt% CuCl/AC and 10.0wt% PdCl$_2$/AC were capable of removing 0.05, 0.223 and 0.327wt% g^s/g$_{ads}$of sulfur adsorption capacity per gram of saturation time, respectivlely. The best adsorbent, 10wt% PdCl2/AC, has sulfur adsorption capacities of 0.221 and 0.327wt% g^s/g$_{ads}$at breakthrough and saturation time, respectively.

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