

Removal of sulfur compounds in FCC raw C₄ using activated carbon impregnated with CuCl and PdCl₂

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Abstract—Fluid catalytic cracking (FCC) is one of the most important refinery processes for economical efficiency that produces commercial fuels with acceptable concentrations of sulfur. Several activated carbon (AC) based adsorbents were studied to develop a more efficient adsorbent for removal of mercaptanes and sulfides during the FCC C₄ refinery process. The adsorbents were prepared by impregnating AC with CuCl and PdCl₂. To evaluate the degree of metal halide impregnation into the AC support, each adsorbent was characterized by N₂ adsorption, elemental analysis (EA) and XRF. Three types of ACs were used to investigate the effect of the structural properties such as surface area, total pore volume and pore size distribution. From this analysis, an AC micro pore size of 0.7 nm was found to be the most effective support material for FCC C₄ removal of sulfur compounds. The experimental adsorption isotherms were compared with Langmuir and Freundlich models and were found to fit the Freundlich model much better than the Langmuir model. The sulfur removal performance of the prepared adsorbents was tested using the breakthrough experiments. The sulfur adsorption capacities of adsorbents decreased in the following order: AC impregnated PdCl₂, AC impregnated CuCl and non-impregnated AC (NIAC). The saturated adsorbents were regenerated by toluene treatment and reactivated at 130 °C under a vacuum.

Key words: Sulfur Removal, Desulfurization, Adsorption, Activated Carbon Adsorbent, CuCl Adsorbent, PdCl₂ Adsorbent, Impregnation, FCC

INTRODUCTION

As the estimated amount of oil deposits continually dwindles and the price of oil continues to increase, it has become necessary to refine crude oil that contains a high sulfur content. The total content of sulfur in oil products is currently much higher than the acceptable limit in some places [1,2]. The sulfur content should be lower than 1.0 ppmw to avoid poisoning the catalysts in the emission control systems of vehicles. The SO_x that is produced from the combustion of oil with a high sulfur content is harmful to human health and it may cause acidic rain. Therefore, there is currently a pressing need for methods that can remove high levels of sulfur from oil. In fact, the U.S. environmental protection agency (EPA) has already issued a mandate that the total sulfur content must be dropped down to 5 and 10 ppmw in diesel and gasoline, respectively, before 2010. Similar stringent new regulations are being implemented in Europe and Japan. Sulfur-free fuel has been a goal in all countries across the world. Various refinery processes are being developed all over the world to produce refined economic and sulfur free commercial fuels.

Among these processes, the FCC process is one of the most economical efficient refinery processes for the conversion of relatively heavy hydrocarbons to lighter hydrocarbons. Some FCC based refin-

eries can lower the level of sulfur during the refinery process by using various catalysts and/or adsorbents. In fact, various desulfurization processes are being developed to remove sulfur compounds from commercial fuels. Of these methods, the hydrodesulfurization (HDS) processes have been most extensively employed to reduce sulfur levels from commercial fuels. However, it is difficult to reduce sulfur levels using the current HDS process because of the very low reactivity of the HDS catalysts towards sulfur compounds [3,4]. An increase in the reactor size and hydrogen consumption is required to achieve high levels of desulfurization [5]. Extensive research has been carried out to find adsorbent materials that are highly selective toward just sulfur compounds. One way to avoid increased costs is to use different approaches like an adsorption process that operates at ambient condition.

Desulfurization of commercial fuels by selective adsorption has been reported as an alternative technology for the current HDS method. Yang and coworkers reported using zeolites for selective adsorption under ambient conditions for the desulfurization of commercial fuels [6-10]. Metal ion-exchange Y zeolites have also been shown to effectively remove sulfur compounds under ambient conditions. However, the sulfur adsorption capacity depends on the composition of the fuel. Adsorptive removal of sulfur compounds from liquid commercial fuels has been widely investigated using various different adsorbents such as porous carbon materials [11,12], metal impregnated oxides [13], zeolite 5A [14], 13X [15,16] and Y zeolites of various metal cation forms [17,18]. Among these adsorbents, Ag-Y and Cu-Y zeolites have been shown to have a particularly high adsorption capacity and selectivity for thiophene and its derivatives via π -complexation. The advantages of using adsorbents, such

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^{*}This paper is dedicated to Professor Jae Chun Hyun for celebrating his retirement from Department of Chemical and Biological Engineering of Korea University.

as the low-energy demands of the process, potential to regenerate the spent adsorbent, and broad availability of adsorbents, have made adsorption processes an attractive area of research. Many research groups have investigated the desulfurization of liquid commercial fuels by adsorption with AC [19-21]. Wang and coworkers have focused on developing a kind of adsorbent that relies on π -complexation bonding to selectively remove organic sulfur molecules from commercial fuels [22]. It was found that AC that was impregnated with metal halides of CuCl/AC or PdCl₂/AC had a high selectivity in the desulfurization of JP-5, a jet fuel that has a high sulfur content (1,172 ppmw S). A significant amount of sulfur removal occurred at about 6.0 ml/g with PdCl₂/AC, which was far greater than other known adsorbents, in jet fuel [22]. When PdCl₂/AC was compared with PdCl₂/Al₂O₃, the support was shown to have an important effect on the performance of adsorbent in the desulfurization of jet fuel. Previous studies have suggested that the sulfur removal capacity can be improved by metal or metal halide impregnation into adsorbents although the feed composition, sulfur content and process conditions are different.

Based on these previous investigations it is clear that sulfur compounds can be removed by adsorption over certain AC impregnated metal halide. However, it is worth noting that the type and content of the sulfur compounds in these applications are rather different. Moreover, the media in which adsorption occurs also varies largely from one case to another. Therefore, it is difficult to make a parallel comparison between different adsorption systems.

In the present study, activated carbon that was impregnated with CuCl (CuCl/AC) and PdCl₂ (PdCl₂/AC) was prepared and examined with the goal of developing an efficient adsorbent for the FCC refinery process. FCC C₄ is the processing material that is refined from heavy oil to obtain a light and economical product. FCC C₄ generally contains sulfur compounds at a concentration of 14.8 ppmw. Our goal is to reduce this level from FCC C₄ to below 1.0 ppmw in order to prepare a refined source of clean fuels. Sulfur adsorption capacities were calculated by Langmuir and Freundlich isotherms to predict the performance of the adsorbents. The effect of the different metal halides that were impregnated in ACs 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 the chemical and structural properties of metal halide impregnated within ACs as adsorbents.

EXPERIMENTAL

1. Preparation of the Adsorbent

Three types of activated carbons (ACs) were used in this study to investigate the effect of the structural properties: K-1 (Kaya Activated Carbon Inc., KOREA), C-1 (Calgon Corporation, USA) and H-1 (Hanil Tech Inc., KOREA). All AC samples were washed with de-ionized water to remove impurities that can form during activation. The washed AC was dried at 130 °C for 12 h in a vacuum to remove residual water and to activate the AC as adsorbents for sulfur adsorption.

A C-1 sample with well-developed micro porosity was chosen as the starting support material to prepare the AC adsorbent that was eventually impregnated with metal halides. The CuCl/AC and PdCl₂/AC were prepared following the incipient wetness method.

First, metal halides, which were dissolved in an HCl solution, were prepared at different amounts of CuCl (99.9%, Aldrich) and PdCl₂ (99.9%, Aldrich). Then, the solution was added to the ACs in the volumetric ratio of 1 : 1 (support material : metal halide solution) and maintained at ambient conditions for 6 h to allow the adsorbent to age. This step facilitates the dispersion of metal halide particles into the pores of the ACs. These samples were washed with de-ionized water and dried in vacuum at 130 °C for 12 h. The entire sample was purged with nitrogen and activated under a helium atmosphere at 130 °C for 3 h before the adsorption experiment.

2. Characterization

The BET specific surface area of NIAC, CuCl/AC and PdCl₂/AC was measured by nitrogen adsorption at 77 K using a micromeritics (ASAP-2020). The BJH, MP and HK method were used to calculate the specific surface area, micro pore volume and pore size distribution of the adsorbents, respectively. Prior to analysis, the samples were degassed at 120 °C for at least 24 h.

X-ray fluorescence (XRF) analysis was used to determine the amount of metal halides that were impregnated in adsorbents by using an X-ray fluorescence spectrometer bench-top multi channel analyzer. The amount of impregnated metal halides was calculated from the peak of the XRF analysis. The system was purged with helium gas at 140 ml/min prior to the flash combustion process. This analysis was repeated three times for each sample to provide an average reading. GC-FPD analysis was performed with an HP 6890 series gas chromatograph, equipped with SUPELCO GAS-PRO sulfur capillary column and flame photometric detector (FPD). All of the FCC C₄ sample was collected at predetermined time intervals depending upon flow conditions that were set for the breakthrough test and nature of the breakthrough curve. These curves were analyzed in the liquid phase using a liquid sampling valve and HP 6890 system to maintain the same compositions of the FCC C₄ feeds. Peak identification of sulfur compounds in the FCC C₄ was carried out using a standard solution [23]. The standard solution was prepared in n-butane with methyl mercaptane (MM), ethyl mercaptane (EM) methyl sulfide (MS), diethyl disulfide (DEDS) and

Table 1. Compositions of FCC C₄

Name	Content (vol%)	S content (ppmw)
Sulfur compound		
Mehtylmercaptane		0.8
Dimethyldisulfide		12.0
Diethylsulfide		0.2
Total		13.0
Unsaturated HC		
1-Butene	16.5	
cis-2-Butene	18.0	
1,3-Butadiene	0.26	
Paraffin		
Propane	0.53	
iso-Butane	33.1	
n-Butane	8.16	
trans-2-Butane	17.8	
Others	5.65	
Total	100.0	

dimethyl disulfide (DMDS) to obtain the calibration data.

3. Reagents

Generally, FCC C₄ is known to contain approximately 14.8 ppmw of sulfur compounds. GC-calibration was performed with a GC-FPD using FCC C₄, which was obtained from the SK Corporation, to accurately determine the composition of the sulfur content of the FCC C₄. Using this analysis the FCC C₄ was shown to actually contain 13.0 ppmw of sulfur compounds. Table 1 shows the composition of the FCC C₄ used in this study. A major sulfur compound of the FCC C₄ was DMDS, which was then used as the target sulfur compound for developing the adsorbent for the selective adsorption process. Fig. 1(a) and (b) show the GC-FPD chromatograms of the standard solution and the FCC C₄, respectively.

4. Adsorption Equilibrium and Breakthrough Experiments

A sulfur adsorption equilibrium experiment was carried out to predict the adsorption performance and the maximum sulfur adsorption capacity of the adsorbents in a stirred batch system at 25 °C and 10 atm, which was the same condition at the FCC refinery process. Under these conditions, the FCC C₄ is in the liquid phase due to the high pressure. Temperature and pressure could be controlled with a water bath and ultra pure nitrogen gas. Different amounts of

adsorbents were weighed and added to the batch reactor that contained 40 ml of the liquid phase FCC C₄, which had an initial sulfur concentration of 13.0 ppmw. The solution was mixed by a magnetic stirrer to efficiently mix the adsorbent and the FCC C₄ for 30 minutes. The FCC C₄ equilibrium samples were collected after 30 minutes by using a liquid sampling valve to calculate the sulfur adsorption capacity of the adsorbents. The FCC C₄ equilibrium samples were injected into the GC-FPD using a liquid sampling valve and the remaining amount of the sulfur compounds in the FCC C₄ was calculated. The sulfur adsorption equilibrium experiment was carried out at least three times to obtain the result.

All dynamic adsorption breakthrough experiments were carried out in a sus-column, which had an 8 mm inside diameter, a 12 mm outside diameter and a column length of 250 mm. The dynamic adsorption experiments were performed at 25 °C and 10 atm to simulate the real FCC refinery process. An up flow condition in all the breakthrough experiments, which was created using an HPLC pump, was used to prevent a channeling effect. The adsorbents were loaded inside the column and pretreated *in situ* using dry nitrogen gas at 130 °C to remove entrapped gases and impurities. After activation treatment, the liquid FCC C₄ was injected into the adsorption column in an up-flow direction using the HPLC pump and a back-pressure regulator, which was used to keep the pressure inside of the column stable. The effluents were collected using a liquid sampling valve and analyzed by the same method described above. The adsorption amounts were obtained using the following Eq. (1) [22], where q is the total amount of absorbed sulfur (mmol/g), v is the feed volumetric flow rate (cm³/min), ρ_f is the fuel density (g/cm³) at room temperature, C_i is the total sulfur concentration in the feed (ppmw S), m_A is the weight of the sorbent bed (g), MW_S is the molecular weight of sulfur and $C(t)$ is the total sulfur concentration of the effluent (ppmw S) at any time t (min). The integral on the right hand side of Eq. (1) is the area above the breakthrough curves at any time t . The breakthrough adsorption amounts were obtained at the point where the total sulfur concentration was less than approximately 0.1 ppmw S.

$$q_{\text{breakthrough}} = \left(\frac{v}{m_A} \right) \left(\frac{\rho_f}{MW_S} \right) \int_0^t \left[\frac{C(t)}{C_i} \right] dt \quad (1)$$

5. Regeneration of the Adsorbent

The regeneration experiments were performed to investigate the efficiency of regenerating the spent adsorbents. The saturated samples were regenerated by washing with toluene to remove the sulfur compounds that were adsorbed to the adsorbents. Toluene consists of one benzene ring and one methyl functional group that can form a π -complexation with the metal halide in the spent adsorbent. Sulfur compounds adsorbed in the spent adsorbents can be removed in this step. The toluene treated adsorbents were dried in a vacuum at 130 °C for 12 h. Finally, all the samples were purged *in situ* under ultra pure nitrogen and reactivated under helium gas at 130 °C for 3 h.

RESULTS AND DISCUSSION

1. The Effect of the Pore Size Distribution of the Support Material

The sulfur adsorption capacity of the adsorbents is related to the

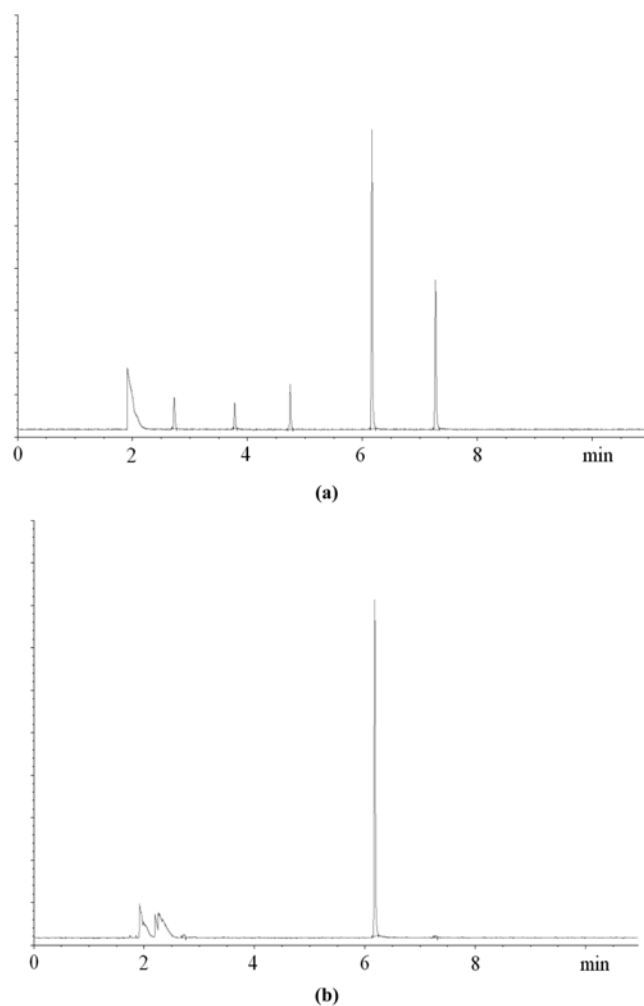
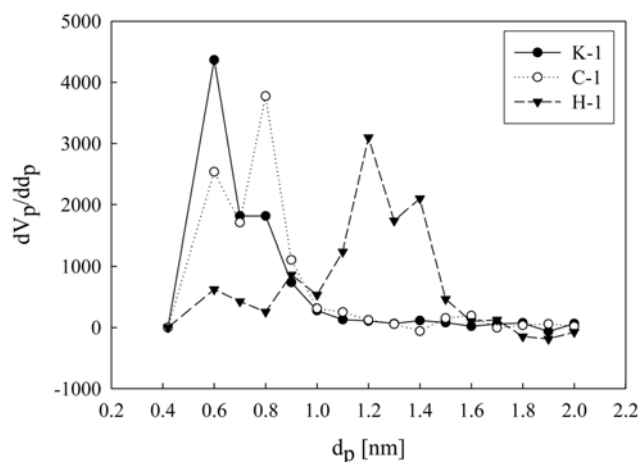


Fig. 1. (a) Standard solution for GC calibration; (b) GC-FPD Chromatogram of FCC C₄ feed.

Table 2. Structural parameters of AC calculated from nitrogen adsorption at 77 K

Sample	BET surface area (m ² /g)	V _{total} (cm ³ /g)	Sulfur adsorption capacity (wt% g ^s /g _{ads})
K-1	1280	0.62	0.019
C-1	964	0.43	0.052
H-1	973	0.44	0.038

**Fig. 2. Pore size distribution of K-1, C-1 and H-1.**

structural properties of the support material such as BET specific surface area, total pore volume and pore size distribution. This is especially true for the pore size distribution, which is a very important factor to consider when selecting the adequate AC as a support material. Adsorption experiments were carried out on three different types of ACs to investigate the relation between the sulfur adsorption capacity and the pore size distribution of the support material. The three types of ACs tested all have different pore size distributions. Table 2 shows the structural properties of the tested ACs and their corresponding sulfur adsorption capacities. Fig. 2 shows the pore size distributions of K-1, C-1 and H-1. As shown in Table 2 and Fig. 2, the adsorption capacity of the adsorbent strongly depended on the pore size distribution of the adsorbent. However, there was a poor correlation between sulfur adsorption capacity and BET specific surface area and total pore volume. In the case of pore diameter, when the adsorbent was slightly larger than the diameter of the adsorbate, the adsorbate was strongly adsorbed due to van der Waals forces. If the pore diameter of adsorbent was smaller than the adsorbates, it could not enter into the pore of the adsorbent. If the pore diameter of adsorbent is much larger than the diameter of the adsorbates, the adsorption interaction forces get weaker and it could readily move in and out without any interruption. As shown in Fig. 2, the major pore width of K-1, H-1 and C-1 was approximately 0.5 nm, 0.7 nm and 1.2 nm, respectively. Since the diameters of MM and DMDS molecules are 0.42 nm and 0.53 nm, the sulfur adsorption capacity was highest in type C-1. This indicates that the physical adsorption forces can be controlled by the energy of the overlapping adsorption potentials. Therefore, one must consider the pore diameter of the adsorbent when developing efficient adsorbents for FCC C₄, where the size needs to be slightly larger than the size of

the sulfur compounds. These results suggest that the sulfur adsorption capacity of AC can be improved by developing more narrow pore size distributions for each sulfur component.

2. Characterization of the Adsorbent

The NIAC, CuCl/AC at various CuCl concentrations and PdCl₂/AC at various PdCl₂ concentrations were prepared using the incipient wetness method and were subsequently used to perform the adsorption equilibrium experiment and breakthrough experiment to assess the efficiency of each of these adsorbent in the FCC refinery process.

The BET specific surface area, total pore volume and pore size distribution of the adsorbents used in this study are listed in Table 3. The BET specific surface areas of CuCl/AC and PdCl₂/AC were reduced from 964.2 m²/g to 794.1 m²/g and 779.5 m²/g, respectively. The total pore volumes were also reduced from 0.43 m³/g to 0.35 m³/g and 0.33 m³/g, respectively. Based on this it appears that the metal halide particles can block and/or fill the pores in the adsorbent material. Nevertheless, the average pore size distribution was almost the same before and after impregnation. The pore size distributions of C-1 before and after impregnation of PdCl₂ are shown in Fig. 3. These results indicate that the adsorbents prepared in this study have a high degree of metal halides that are dispersed in the

Table 3. Structural parameters of metal CuCl/AC and PdCl₂/AC calculated from nitrogen adsorption at 77 K

Sample	BET surface area (m ² /g)	V _{total} (cm ³ /g)	Sulfur adsorption capacity (wt% g ^s /g _{ads})
NIAC	964.2	0.43	0.052
2.5 wt% CuCl/AC	904.8	0.40	0.167
5.0 wt% CuCl/AC	858.6	0.37	0.194
10.0 wt% CuCl/AC	794.1	0.35	0.223
15.0 wt% CuCl/AC	713.2	0.31	0.219
2.5 wt% PdCl ₂ /AC	896.2	0.40	0.242
5.0 wt% PdCl ₂ /AC	848.4	0.36	0.286
10.0 wt% PdCl ₂ /AC	779.5	0.33	0.327
15.0 wt% PdCl ₂ /AC	703.2	0.29	0.312

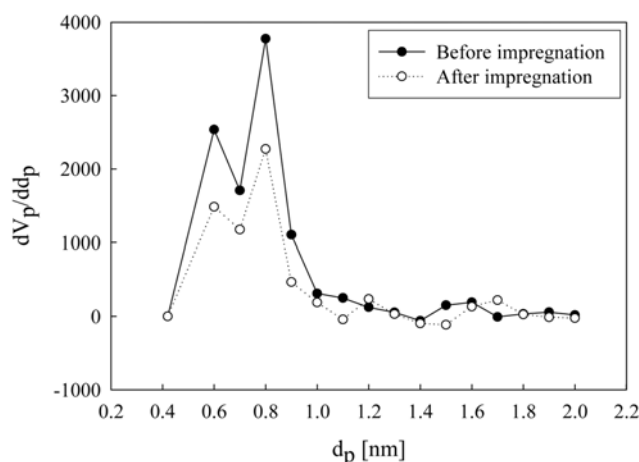
**Fig. 3. Pore size distribution of C-1 before and after impregnation of 10 wt% PdCl₂.**

Table 4. Elemental 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
5.0 wt% PdCl ₂ /AC	73.74	1.82	0.45	22.66

AC support.

The content of CuCl and PdCl₂ in the adsorbents was analyzed by XRF. The peak intensity of CuCl in CuCl/AC clearly increased from 25.76 cps for NIAC to 4,119.2 cps and the peak intensity of PdCl₂ of PdCl₂/AC increased from 0.00 cps to 181.2 cps. This shows that CuCl and PdCl₂ particles were successfully impregnated in the AC.

Table 4 shows the results of the elemental analysis of NIAC, 5.0 wt% CuCl/AC and 5.0 wt% PdCl₂/AC. After impregnation of CuCl and PdCl₂, the content of C (carbon), H (hydrogen) and N (nitrogen) decreased from 80.35% for NIAC to 74.79% for 5 wt% CuCl/AC and 73.74% for 5 wt% PdCl₂/AC, while other elements including the CuCl and PdCl₂, increased from 16.41% for NIAC to 20.88% for 5 wt% CuCl/AC and 22.66% for 5 wt% PdCl₂/AC. This result verifies the successful introduction of metal halide into the AC.

3. Adsorption Isotherms

The adsorption equilibrium experiments of the sulfur compounds in FCC C₄ were performed on the NIAC, 10.0 wt% CuCl/AC and 10.0 wt% PdCl₂/AC. Adsorption isotherms are essential for the description of how adsorbates will interact with impregnated AC. In addition, these isotherms are useful in optimizing the sulfur adsorbent capacity of impregnated AC [24-26]. Adsorption isotherms for the CuCl/AC and PdCl₂/AC are shown in Figs. 4 and 5, respectively. The obtained results at equilibrium were fit to Freundlich and Langmuir isotherm models. The Freundlich isotherm is an empirical model that can be applied to non-ideal adsorption on heterogeneous sur-

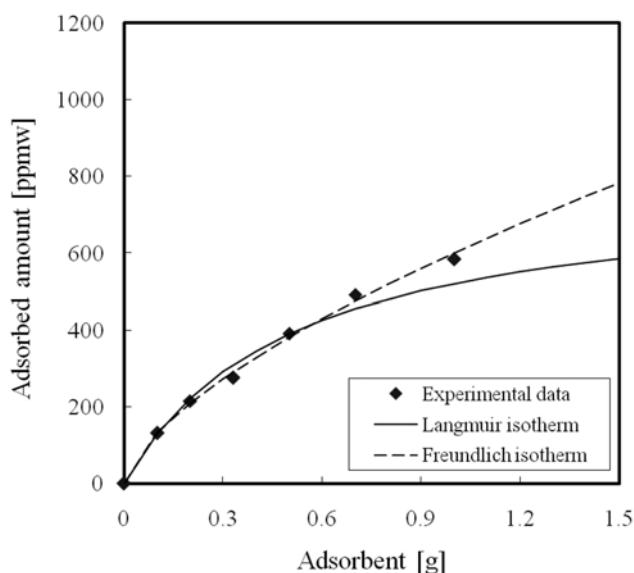


Fig. 4. Adsorption isotherm of sulfur compounds in FCC C₄ of 10 wt% CuCl/AC at 25 °C and 10 atm.

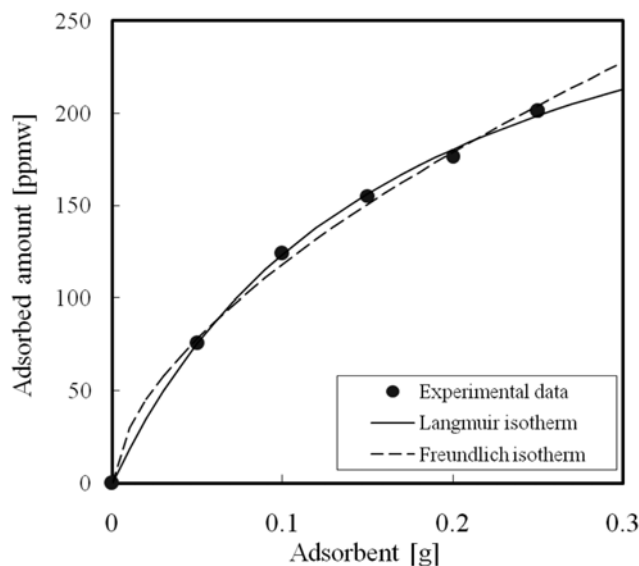


Fig. 5. Adsorption isotherm of sulfur compounds in FCC C₄ of 10 wt% PdCl₂/AC at 25 °C and 10 atm.

faces as well as multilayer adsorption. Its formula is shown in Eq. (2) which relates the uptake, q (mg S/g), to the concentration in solution, C (ppmw S).

$$q = q_m C^n \quad (2)$$

Where q_m is the Freundlich adsorption constant ((g/μg)^{1/n}) and n is the Freundlich exponent. The equation that describes the Langmuir model is shown in Eq. (3):

$$q = \frac{q_m B C}{1 + B C} \quad (3)$$

Where B is Langmuir adsorption constant (g/μg), q_m is the adsorption capacity (mg/g), C (ppmw S) is the concentration in solution and $q_m B$ is the relative affinity of the adsorbate toward the surface of the adsorbent. Freundlich and Langmuir isotherm parameters are listed in Table 5. Both adsorbents fit the Freundlich isotherm better than the Langmuir isotherm since the regression coefficient of the Freundlich isotherm was closer to 1.0 than that of the Langmuir isotherm. The Freundlich model takes into account surface heterogeneities; thus, the good fit of this model with the experimental data suggests the sulfur is selectively adsorbing onto the CuCl/AC and PdCl₂. The sulfur adsorption capacity of each adsorbent as determined through the breakthrough experiments was predicted by the Freundlich isotherm. In addition, the adsorption capacity of

Table 5. Langmuir and Freundlich parameters for adsorption of CuCl/AC and PdCl₂/AC at simulated FCC refinery conditions

	Langmuir constants			Freundlich constants			
	q_m (mg/g)	K (10 ⁻³)	R^2	q_m (mg/g)	n	$1/n$	R^2
CuCl/AC	782.35	1.98	0.989	600.64	1.53	0.65	0.995
PdCl ₂ /AC	334.80	5.95	0.954	465.91	1.68	0.60	0.993

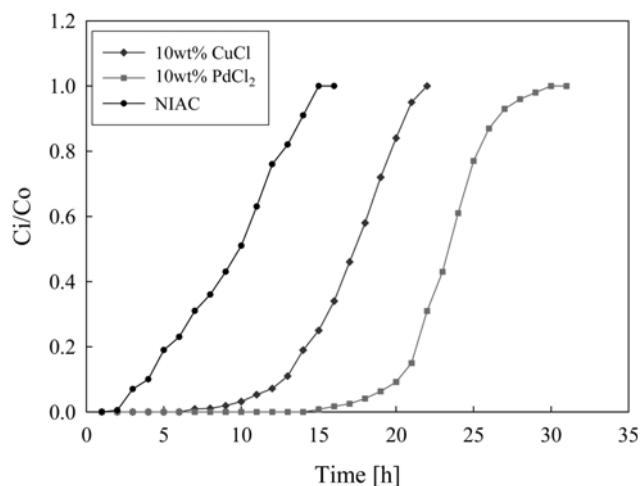


Fig. 6. Breakthrough curves in FCC C₄ feed with NIAC, 10 wt% CuCl/AC and 10 wt% PdCl₂/AC.

PdCl₂/AC was greater than CuCl/AC (Fig. 4 and 5). Although the metal halide content of the adsorbents was the same, the sulfur adsorption capacity can be changed by the presence of the impregnated metal halides. These results show that the PdCl₂/AC is more selective toward sulfur compounds in FCC C₄ than CuCl/AC.

4. Breakthrough Experiments of Adsorbent

Breakthrough experiments were also used to investigate the effect of metal halide impregnation on sulfur removal at conditions that simulate the FCC refinery process.

Fig. 6 shows the breakthrough and saturation curves of total sulfur compounds in FCC C₄ with NIAC, CuCl/AC and PdCl₂/AC. These adsorbents were capable of removing 0.052 wt% g^s/g_{ads} for NIAC, 0.221 wt% g^s/g_{ads} for CuCl/AC and 0.327 wt% g^s/g_{ads} for PdCl₂/AC of sulfur adsorption per gram of saturation time. The total amount of adsorbed sulfur compounds for each adsorbent can be calculated by Eq. (1). Fig. 6 shows that there are large differences in the adsorption behavior of these samples. Compared to NIAC, ACs impregnated with metal halides had much higher sulfur adsorption capacities. Impregnation of metal halides can improve the sulfur adsorption capacity via the interaction between the sulfur compound and adsorbent. Fig. 6 also shows the difference in the sulfur adsorption capacity between CuCl/AC and PdCl₂/AC. The interactions between the sulfur compounds and the adsorbent strongly depended on the type of metal halides in the adsorbent. The sulfur adsorption capacity of PdCl₂/AC was almost 2 times higher than that of CuCl/AC. These results coincide well with the prediction of the Freundlich isotherm in Fig. 5. From the above results, PdCl₂/AC had a higher sulfur adsorption capacity than NIAC and CuCl/AC.

In a recent study, Yuhe Wang examined the sulfur removal capabilities of CuCl/AC and PdCl₂/AC. Sulfur compounds in the fuel were about 400 ppmw and consisted of thiophene derivatives [23]. Their results showed that the sulfur adsorption capacity of PdCl₂/AC was higher than that of CuCl/AC. Since there were large differences between their study and this study, such as species, sulfur concentration, feed composition and experimental conditions, it is hard to directly compare these results. However, in the aspect of the adsorption tendency of each adsorbent in Fig. 6, this study is in agree-

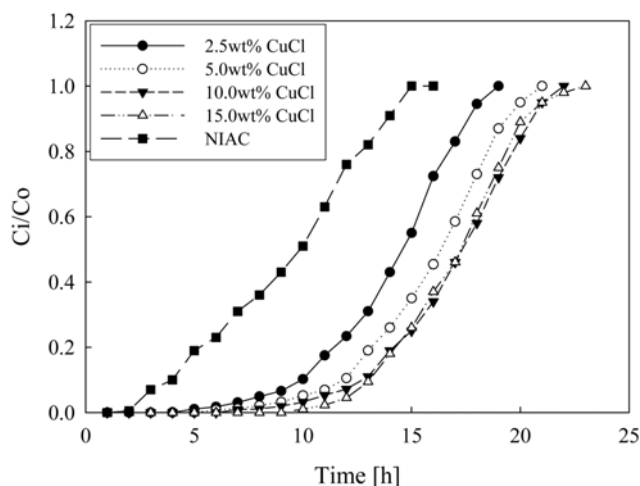


Fig. 7. Breakthrough curves in FCC C₄ feed of CuCl/AC at various concentrations of CuCl.

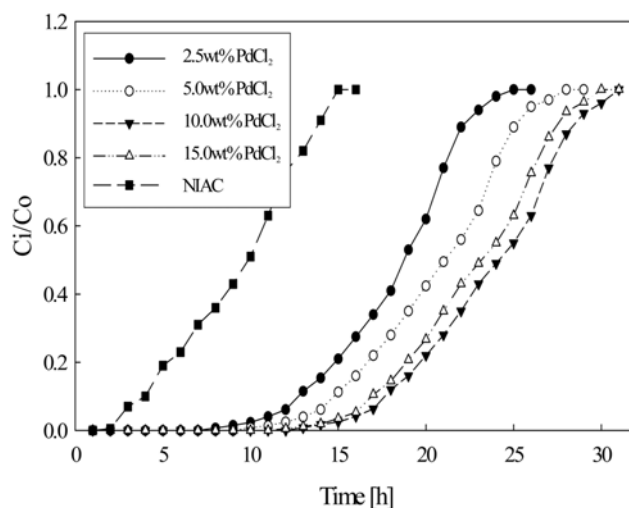


Fig. 8. Breakthrough curves in FCC C₄ feed of PdCl₂/AC at various concentrations of PdCl₂.

ment with the study of Wang and previous studies [23].

CuCl/AC at various CuCl concentrations and PdCl₂/AC at various PdCl₂ concentrations were used to investigate the effect of the metal halide concentration at conditions that simulate the FCC refinery process. Figs. 7 and 8 show the breakthrough and saturation curves at the different CuCl and PdCl₂ concentrations. The results are shown in Table 3. The sulfur adsorption capacity of 10.0 wt% CuCl/AC was much higher than NIAC and 2.5 wt% CuCl/AC. In addition, the amount of metal halide was found to affect the structural properties and performance of the adsorbent. Remarkable changes in structural properties such as BET specific surface area, total pore volume and pore size distribution were observed after impregnation of different concentrations of the metal halides. In the case of the 10.0 wt% CuCl/AC, the total pore volume decreased from 0.43 cm³/g to 0.35 cm³/g and the specific surface area decreased from 964.2 m²/g to 794.1 m²/g when the concentration of impregnated CuCl increased. However, the performance of the 10.0 wt% CuCl/AC was still higher than NIAC. This result can be explained by the

structural effect and chemical interaction that is caused by the impregnation of different amounts of metal halides. At the low metal halide concentrations, the sulfur adsorption capacity of the adsorbents increased with the metal halide concentration. Although there was some loss in adsorption capacity from the decrease in surface area and total pore volume, the overall sulfur adsorption capacity increased due to the chemical interaction force between the sulfur compounds and the CuCl content of the adsorbents. However, the sulfur adsorption capacity slightly increased or decreased when the metal halide concentration was above a certain threshold. In the case of 15 wt% CuCl/AC, the sulfur adsorption capacities slightly decreased due to the negative effect of the impregnated metal halide on the structural properties, although the amount of impregnated CuCl increased. These results demonstrate that the negative effects of the impregnated metal halide on the structural properties start to get larger than the positive effects when the metal halide content is above 10.0 wt%. This indicates that there are some trade-off effects between the amount of impregnated metal halides and the sulfur adsorption capacity. Therefore, the sulfur adsorption capacity can be controlled by choosing an appropriate concentration of the metal halide for FCC C₄.

5. Regeneration of Adsorbent

The spent AC can be regenerated by various methods such as thermal [27,28], ozone [29], ultra sound [30] and solvent regeneration [31,32]. This is especially true for thermal regeneration, which is widely used for regeneration of spent AC. However, the adsorption capacity of the AC can decrease as a result of the loss of structural properties by carbonization or blocking of the pores in the AC after thermal treatment.

The spent 10 wt% CuCl/AC and 10 wt% PdCl₂/AC were used for regeneration experiments after saturation during FCC C₄. The results of the regeneration experiment with FCC C₄ are shown in Fig. 9. There was no change of color, smell and shape after the adsorption experiment. Thus, the regeneration efficiency of adsorbent was investigated by calculating the sulfur adsorption capacity after the regeneration treatment. From these experiments, the sulfur ad-

sorption capacities of regenerated 10 wt% CuCl/AC and regenerated 10 wt% PdCl₂/AC in FCC C₄ were found to be 0.138 wt% g/g_{ads} and 0.213 wt% g/g_{ads}, which were almost 62% and 65% of the initial value, respectively. The sulfur adsorption capacities of regenerated adsorbents decreased as the number of regeneration cycles increased. Approximately 65 and 54% of the sulfur adsorption capacities of PdCl₂/AC were recovered after the first and second regeneration treatments, respectively.

CONCLUSION

ACs impregnated with metal halides were prepared and examined with the goal of developing efficient adsorbents for the FCC refinery process. The sulfur adsorption capacity of AC was improved by developing narrow pore size distribution for each sulfur component. We found that the C-1, which had a pore diameter 0.7 nm, was the most effective FCC C₄ adsorbent material in removing sulfur compounds. CuCl/AC and PdCl₂/AC were successfully prepared to investigate the effect of the type of halide metal and concentration in halide metal impregnated ACs on sulfur removal. Both adsorbents fit the Freundlich model better than Langmuir model. The sulfur adsorption capacity of the adsorbents decreased in the following order: PdCl₂/AC, CuCl/AC and NIAC, where 10 wt% PdCl₂/AC had the highest level of sulfur removal. These results corresponded well with the predictions of the Freundlich model. There were some trade-off effects between the amount of impregnated metal halide and the sulfur adsorption capacity of the adsorbent material. The saturated adsorbents could be regenerated with toluene treatment, and about 65 and 54% of the sulfur adsorption capacity was recovered after first and second regeneration treatment.

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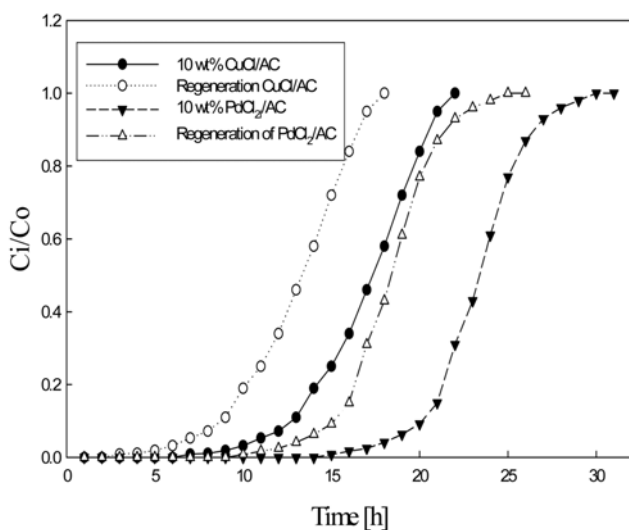


Fig. 9. Breakthrough curves in FCC C₄ feed with the spent 10 wt% CuCl/AC and the spent 10 wt% PdCl₂/AC.

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