

제올라이트 A를 이용하여 이소프렌에서 아세틸렌 제거를 위한 선택적 흡착공정 개발

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Development of Selective Adsorption Process with Various Pore Size A-type Zeolite on Removal of Acetylenes for Isoprene Purification

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본 연구는 이소프렌에서 아세틸렌 불순물을 선택적으로 제거하기 위한 효과적인 흡착제의 개발이다. 흡착제로 기공의 크기가 4 Å에서 5 Å인 제올라이트를 이용하여 아세틸렌을 흡착하여 제거하는데 기공의 크기가 미치는 영향을 살펴보았다. 제올라이트 A의 기공크기는 Na와 Ca의 조성을 변화하여 조절하였다. 특히 아세틸렌의 주성분인 2-methyl-1-butyne-3-yne (IPA)와 2-butyne의 동역학적 지름의 차이 때문에 흡착제의 기공 크기는 흡착효과에 지대한 영향을 미치게 된다. 기공의 크기가 5 Å인 흡착제는 2-butyne의 높은 흡착력을 보였으나 IPA에는 낮은 흡착력을 보였다. 흡착등온선의 경우 개선된 Langmuir 모델이 2-butyne 흡착에 대해서 가장 좋은 fitting을 보였다. 이외에도 최적의 재생 조건을 찾기 위한 실험을 수행하였고 300 °C에서 12 h 동안 재생하였을 때 매우 효과적이었다.

This study focused on the development of effective adsorbent to remove acetylenes for the purification of isoprene. The adsorbents with various pore sizes from 4 Å to 5 Å were prepared to investigate the effect of pore size on selective adsorption of acetylene as an impurity. The pore size of zeolite A was adjusted by ion-exchange between Na and Ca ions. The pore size of adsorbents has affected the removal of acetylenes selectively because of the kinetic diameter of acetylenes, such as 2-methyl-1-butyne-3-yne (IPA) and 2-butyne. In a batch adsorption experiment, 5A zeolite with pore size of 5 Å showed the highest removal capacity of 2-butyne. However, IPA was hardly removed from isoprene by the A-type zeolites. For the adsorption isotherm, modified Langmuir model was well fitted with 2-butyne adsorption. Moreover, the regeneration of adsorbent was carried out to determine optimum method. The adsorbent heated for 12 h at 300 °C was regenerated significantly.

Keywords: adsorption, isoprene, acetylenes, A zeolite

1. Introduction

Refinery streams contain a broad spectrum of olefinic compounds produced from either catalytic cracking or thermal cracking processes. Many of these compounds are valuable, especially as feed stocks for chemical products. Usually, a small amount of acetylene (less than 3%) is present in the stocks. Since the acetylenes are main inhibitor i.e. olefin polymerization, removal of acetylenes from olefin compounds is an important process in the large-scale polymer production[1,2]. For the reason, the concentration of acetylenes should be reduced to less than

10 ppm in a commercial process. Conventionally, distillation process has been employed on removal of acetylenes from hydrocarbon mixture[3]. However, this process is not suitable recently for higher energy consumption to achieve such a low level of purification. The other process, especially for polymer grade ethylene, is selective hydrogenation with novel metal catalysts[4-7]. In regard to the acetylene hydrogenation, the process should be highly selective. When the acetylene concentration is low, the ethylene hydrogenation reaction becomes significant to causes higher ethylene losses.

Recently, the demand of olefinic hydrocarbons (C₄~C₅) has been increased significantly as a raw material for several chemical products. Especially, isoprene is a valuable chemical as a feed in polymer proc-

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ess to manufacture polyisoprene (synthetic rubber). In the naphtha cracking process, isoprene mixture with acetylene as an impurity was produced in side products. Usually the mixture was consumed as a cheaper fuel. Hence, the purification of isoprene to remove acetylenes has been studied to yield more valuable products.

In this work, we have focused on development of high performance adsorbent to remove acetylenes, such as isopropenyl acetylene (IPA) and 2-butyne, from isoprene by adsorption process. Specifically, A-type zeolites with different pore size have been prepared to investigate the influence of pore size on the removal of acetylene, especially 2-butyne. The capability of adsorbents was performed in liquid phase batch-adsorption unit.

2. Experimental

The hydrocarbons, isoprene (99%), 2-methyl-1-butyne-3-yne (IPA, 99%), 2-butyne (99%), 2,2,4-tri-methyl-pentane (TMP, 99.8%) have been supplied from Aldrich Co. and used without further purification. 1 M solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Samjun Chem. Korea, 98.5%) was used for ion-exchange. As an adsorbent, A zeolites were obtained from Aldrich.

X-ray powder diffraction (XRD) pattern of catalysts was recorded using X-ray diffractometer (Shimadzu XRD-6000) operated at 40 kV and 30 mA, using $\text{Cu K}\alpha$ ($\lambda = 0.15418$ nm) radiation to determine the crystal structure. The N_2 adsorption-desorption measurements were performed at 77 K using automated gas sorption system (M/S. Micromeritics ASAP 2000) utilized with Brunner-Emmett-Teller (BET) calculation for the surface area. The sample has been pre-treated at 200 °C for 2 h before analyzing the sample. Observation with FE-SEM (HITACHI S-4200) for the samples was carried out at an accelerating voltage of 15.0 kV. Elemental analysis of the catalysts was performed by inductively coupled plasma (ICP).

Adsorption experiments were carried out in batch conditions at room temperature and atmospheric pressure. The adsorbent (1 g) was activated in the oven at 200 °C for 2 h in the vial. After then, liquid phase feed materials (10 g) were added in the vial. The adsorption vial was shaken for 24 h at 20 °C. The composition of the starting liquid mixtures and the samples withdrawn after adsorption were analyzed in a gas chromatograph with a flame ionization detector using an Agilent HP-5 column (5% phenyl methyl siloxane, 30 mm \times 320 mm \times 0.25 mm).

The regeneration of used 5A zeolite was conducted by two methods, low pressure suction and high temperature calcination. For low pressure suction, the used adsorbents were kept under 10^{-4} torr with at various temperatures, from 30 to 50 °C controlled by water bath. In the high temperature calcination process, the used adsorbents were set in a furnace with air and calcined with a heating rate of 5 °C/min from room temperature to different temperatures and time for burning off the organics. After the regeneration, the adsorbent was used for adsorption experiment without any activation.

Table 1. Physicochemical Properties of Adsorbents

Adsorbent	Na/(Na+Ca) (%)	Ca/(Na+Ca) (%)	BET surface area (m^2/g)	Pore volume (cc/g)
4A	100	0	407	0.28
4.5A	53.2	46.8	414	0.28
5A	25.3	74.7	434	0.25

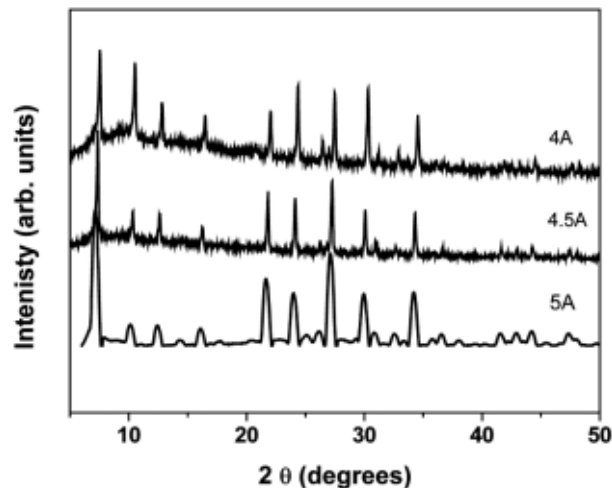


Figure 1. XRD pattern of adsorbents with various pore sizes.

3. Results and Discussion

3.1. Characterization

It is well known that the pore size of zeolite A was determined by composition of cations on the framework consisting pore opening. Generally, 4A zeolite with pore size 4 Å contains Na ion, on the other hand 5A zeolite with pore size 5 Å does mainly Ca ion (more than 80%). Na ion of 4A zeolite was partially exchanged with Ca ion to prepare adsorbents with pore size 4.5 Å. The ion-exchange of 4A zeolite was performed by calcium nitrate solution for 8h. The duration of ion-exchange was optimized to obtain A type zeolite with desirable cation composition. The results of elemental analysis over the adsorbents are presented in Table 1. The ratio of Na to Ca over 4.5A sample was almost unity. The result could confirm the pore size of 4.5A sample.

The crystalline phase of adsorbents was presented in Figure 1. Unmodified adsorbents, 4A and 5A samples, showed their own XRD patterns. However, the XRD pattern of 4.5A sample was transitional state between 4A sample and 5A sample. The three peaks between 10 and 20 of 2 theta value were changed gradually as shown in Figure 1.

The structural properties, BET surface areas and pore volume, of adsorbents are illustrated in Table 1 as well. All zeolites (4A, 4.5A, 5A) showed comparable structural properties. However, BET surface areas were increased with increasing Ca ion composition.

The SEM image indicates the morphology of the adsorbents as presented in Figure 2. The morphology of A type zeolite was cubic. Considering those results, there was small structural effect except pore

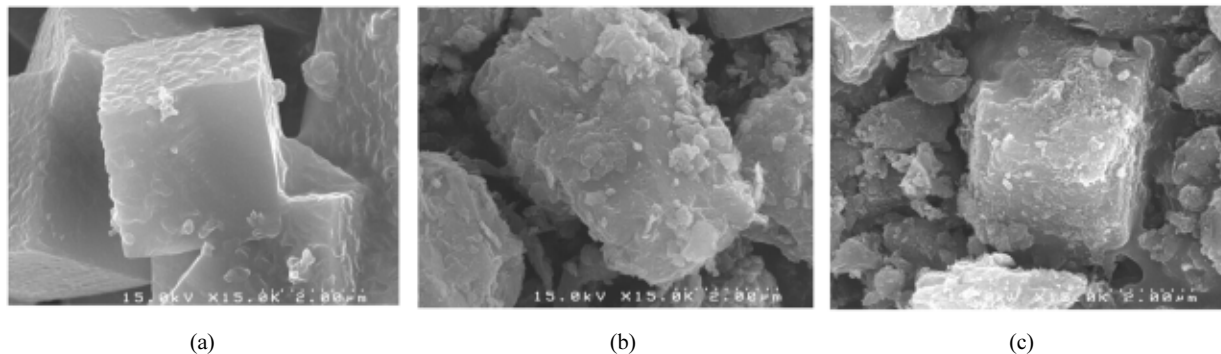


Figure 2. SEM image of adsorbents (a) 4A, (b) 4.5A and (c) 5A.

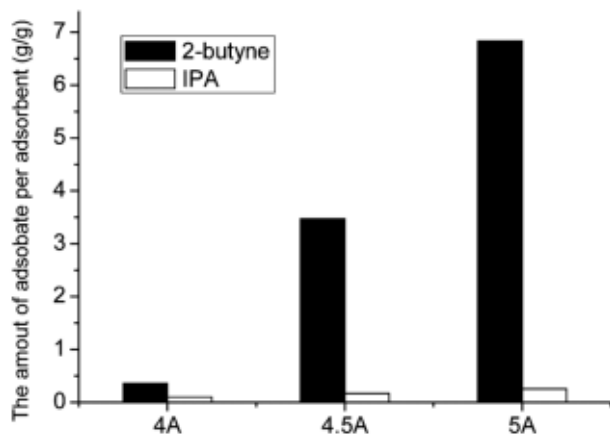


Figure 3. The amount of acetylenes per adsorbent with various pore sizes.

size to determine adsorption capability among all samples used in this work.

3.2. Adsorption Test

The adsorption capability of acetylenes over the adsorbents with various pore sizes was investigated with 2-butyne and IPA. The concentration of acetylene was adjusted to 1000 ppm in 2,2,4-TMP solution as a feed solution. The amount of acetylene adsorbed over zeolites was changed with the pore size of adsorbent as shown in Figure 3. The adsorption of 2-butyne was increased with increasing pore size of adsorbent. 2-butyne with kinetic diameter about 4.3 Å could access to the inside pore of adsorbent with relatively larger pore size. For the other acetylene, IPA, the adsorption capability with pore size of adsorbent was not comparable with 2-butyne. The kinetic diameter of IPA is about 5 Å. For the reason, little IPA was adsorbed over the adsorbent with pore size less than 5 Å.

In previous experiment, 5A sample could be considered as an effective adsorbent to remove 2-butyne. To develop a real adsorption process, 1000 ppm of 2-butyne was prepared in isoprene with same kinetic diameter of IPA. 2-butyne adsorption performance of adsorbent with various pore sizes is shown in Figure 4. Unlike 2,2,4-TMP as a feed solution, the competitive adsorption between 2-butyne and IPA was increased with pore size of adsorbents. Especially, the adsorbents with

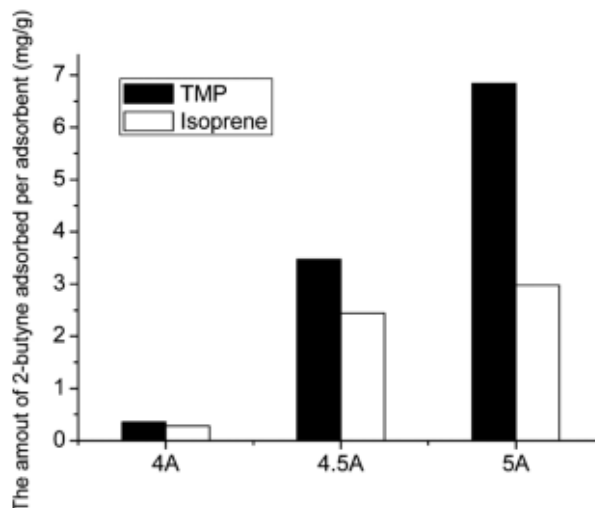


Figure 4. The amount of 2-butyne in different feed solutions per adsorbent with various pore sizes.

pore size of higher than 5A hardly adsorbed 2-butyne due to the competitive adsorption.

3.3. Isotherm Analysis

For the scale up of adsorption process to remove 2-butyne over 5A sample, isotherm equation should be determined precisely. There are popular models for adsorption; Langmuir model and Freundlich model. The conventional Langmuir model is defined as follows.

$$q = \frac{c1 \times C_e}{1 + c2 \times C_e}$$

The other popular model is Freundlich model and it is defined as follows.

$$q = c1 \times C_e^{c2}$$

We tried to fit the data using these two models. We used nonlinear least-squared (nls) method to fit the data with a statistical programming language R (<http://www.r-project.org>). We tried to fit the model with several different initial values and the get the best results. However,

Table 2. Estimated Constants of Isotherm Equilibrium Equations

Model	c1	c2	c3	R-square
Langmuir	0.0504	0.0178		0.9716
Freundlich	0.5577	0.2376		0.9379
M-Langmuir	0.6026	0.0265	0.0088	0.9918

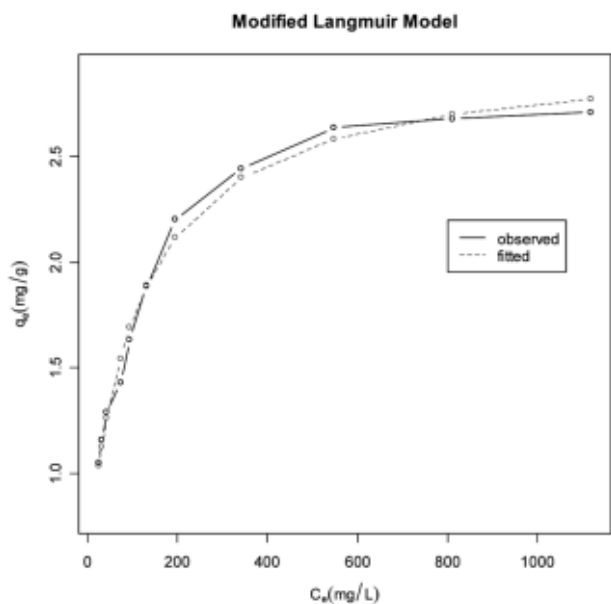


Figure 5. Comparison of estimated result with experimental data for 2-butyne adsorption over 5A sample.

the results were consistent even if we used different initial values unless they are very far from true values. As we can see from Table 2, Langmuir model has a higher R-square value than that of Freundlich model. Therefore, we can say that Langmuir model has a better fit for our data. We like to improve the model fitting, so we modified Langmuir model by adding a constant term in the numerator in Langmuir model. The modified Langmuir model is defined as follows.

$$q = \frac{c1 + c2 \times C_e}{1 + c3 \times C_e}$$

Since this model has a constant term (intercept term) in the numerator, the model flexibility is higher than that of the conventional Langmuir model. Although there is one more parameter to fit, the model fitting can be done without any problem because we have enough data points. As we can see in Table 2, the fitting is improved and R-square value is very high (0.9918). Figure 5 shows the observed value and fitted value for this modified Langmuir model. As we can see, the fitted values are very close to the observed values. Although we do not show the graph for the conventional Langmuir model, the conventional Langmuir model has a bias in small and large values for C_e . We believe this modified Langmuir model can explain our experiment very well.

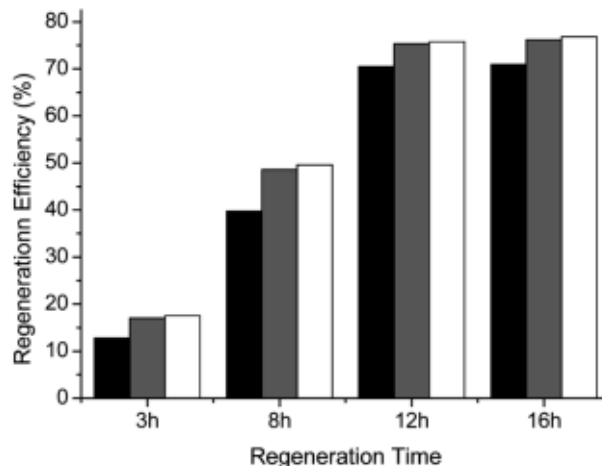


Figure 6. The regeneration efficiency of 5A zeolite with various regeneration time and temperature under vacuum condition (10^{-4} torr). (Black) 30 °C, (Gray) 40 °C and (White) 50 °C.

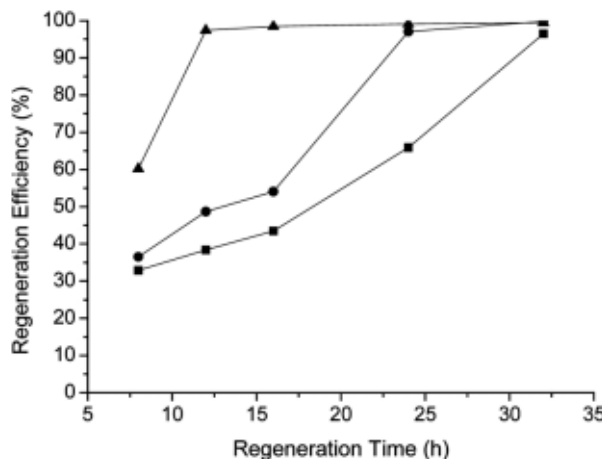


Figure 7. The regeneration efficiency of 5A zeolite with various regeneration time and temperature at atmosphere pressure; (■) 100 °C, (●) 150 °C and (▲) 300 °C.

3.4. Regeneration

In the adsorption process, the regeneration of adsorbent is crucial step for commercialization. Two methods were used in the study to determine optimum regeneration process. In vacuum method, the regeneration efficiency was affected significantly by regeneration time as shown in Figure 6. The efficiency was increased for 12 h after then there was little improvement with increasing regeneration time. The maximum regeneration efficiency was less than 80%. This means the method is not suitable for commercialization. In high temperature calcinations method, the regeneration temperature and time should be considered as a major factor to determine optimum conditions. With increasing regeneration temperature, the regeneration time could be reduced to remove the organics deposited inside adsorbents as shown in Figure 7. Indeed, the adsorbent was regenerated completely by calcination for 12 h at 300 °C.

The calcination regeneration was repeated to investigate the life time of adsorbents. The used 5A zeolite was heated for regeneration at 150

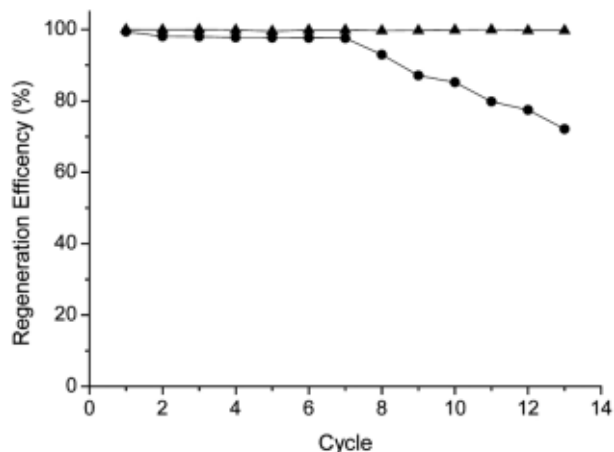


Figure 8. The regeneration efficiency of 5A zeolite with various regeneration time and temperature at atmosphere pressure; (●) 150 °C for 24 h and (▲) 300 °C for 12 h.

°C and 300 °C for 24 h and 12 h, respectively. The life time of adsorbents was illustrated in Figure 8. The adsorbent regenerated at 150 °C was deactivated after 7 cycles. However, the adsorbent was maintained the adsorption capability by calcination at 300 °C for 12 h without any deactivation. This is mainly attribute to the complete removal of adsorbed materials inside zeolite pore at this temperature.

4. Conclusion

The effect of pore size on acetylene removal was studied over adsorbents with various pore sizes between 4A and 5A. The adsorption performance was significantly affected by pore size due to the difference of kinetic diameter in feed materials. 2-Butyne with relatively small kinetic diameter was adsorbed over adsorbent with pore size smaller than 5A. However, IPA was hardly adsorbed over adsorbent with pore size less than 5A. Moreover, main feed solution had affected on the 2-butyne adsorption. Indeed, adsorption of 2-butyne in the isoprene was less than that in the TMP due to competitive adsorption. In isotherm equation, modified Langmuir model was well predicted with less than 1% error for adsorption of 2-butyne over 5A sample. For the regeneration process, the adsorbent was reactivated effectively by heat treatment.

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