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กองทุนรัชดาภิเษกสมโภช

รายงานวิจัย

ชื่อโครงการวิจัย
การแยกโพรเพนและโพรพิลีนโดยกระบวนการดูดซับด้วยซีโอไลต์
ประเภทฟอจาไซต์ที่ประกอบด้วย Cu^+

โดย

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กิตติกรรมประกาศ

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ชื่อโครงการวิจัย	การแยกโพรเพนและโพรพิลีนโดยกระบวนการดูดซับด้วยซีโอไลต์ ประเภทฟอจาไซต์ที่ประกอบด้วย Cu+
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บทคัดย่อ

งานวิจัยนี้ได้ศึกษาผลของการรีดักชันต่อการสังเคราะห์คอปเปอร์(I)เอ็กซ์ และ คอปเปอร์(I)วายซีโอไลต์ และผลของกระบวนการดูดซับโพรพิลีนด้วยซีโอไลต์ที่เตรียมขึ้น ในการเตรียมซีโอไลต์ข้างต้นทำโดยการแลกเปลี่ยนประจุจากโซเดียมเอ็กซ์ และ โซเดียมวายซีโอไลต์ ด้วยสารละลายคอปเปอร์ในแอมโมเนียก่อนที่จะผ่านวิธีการรีดักชันที่ต่างกันสามชนิดดังต่อไปนี้ การไหลผ่านตัวดูดซับด้วยไอของแอมโมเนียเป็นเวลา 1 ชั่วโมง การไหลผ่านตัวดูดซับด้วยไอของแอมโมเนียเป็นเวลา 2 ชั่วโมง และการไหลผ่านตัวดูดซับด้วยก๊าซ ไฮโดรเจนเป็นเวลา 1 ชั่วโมง ผลจากเทคนิค อินดักทีฟลี คัมเป็ล พลาสมา (ไอซีพี) พบว่าการแลกเปลี่ยนประจุระหว่าง คอปเปอร์ และ โซเดียมในโครงสร้างของซีโอไลต์เกิดขึ้นไม่สมบูรณ์ ซึ่งอาจเป็นผลมาจากข้อจำกัดของกระบวนการสังเคราะห์ตัวดูดซับ ผลจากเทคนิค เอ็กซ์เรย์โฟโตอิเล็กตรอนสเปกโทรสโกปี (เอ็กซ์พีเอส) พบว่า ซีโอไลต์ที่ผ่านวิธีการรีดักชันทั้งสามชนิดมีคอปเปอร์(I) รวมอยู่กลับ คอปเปอร์(II) บนโครงสร้างของซีโอไลต์ ได้มีการทดลองโดยใช้เทคนิคเบรคทรูสำหรับศึกษากระบวนการดูดซับโพรพิลีนของตัวดูดซับที่เตรียมขึ้น ซึ่งผลการทดลองพบว่า ตัวดูดซับเลือกดูดซับโพรพิลีนซึ่งเป็นผลของ ไพ คอมเพล็กซ์ ที่เกิดขึ้นระหว่าง คอปเปอร์(I) และ โพรพิลีน นอกจากนี้ยังพบว่าปริมาณการแลกเปลี่ยนประจุบนโครงสร้างของซีโอไลต์มีผลต่อ ไพ คอมเพล็กซ์ ที่เกิดขึ้นในกระบวนการดูดซับโพรพิลีน ได้มีการนำตัวดูดซับที่ผ่านกระบวนการการดูดซับแล้วมาใช้ใหม่เพื่อทดสอบความคงทนและความสามารถในการนำกลับมาใช้ใหม่ของตัวดูดซับ จากผลการทดสอบแสดงให้เห็นว่า ความสามารถในการดูดซับโพรพิลีนของตัวดูดซับลดลง ยิ่งไปกว่านั้น คอปเปอร์(I) บนโครงสร้างของคอปเปอร์(I)วายซีโอไลต์ มีความคงทน น้อยกว่า คอปเปอร์(I) บนโครงสร้างของคอปเปอร์(I)เอ็กซ์ซีโอไลต์หลังจากผ่านการใช้เป็นตัวดูดซับ

Project Title	Propane/propylene separation by adsorption using Cu ⁺ on faujasite zeolites
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Abstract

Effects of three different reduction environments on the preparation of Cu(I)X and Cu(I)Y zeolites and their adsorption selectivities towards propylene were investigated. NaX and NaY zeolites were ion exchanged with ammoniacal copper solution before they were reduced with 1 h of ammonia flow, 2 h of ammonia flow, or 1 h of hydrogen flow. Results from inductively couple plasma indicated that there was an incomplete exchange between Cu⁺ and Na⁺, which may be from the limitation of this preparation method. The x-ray photoelectron spectroscopy results showed that all reduction methods provided the zeolite with the amount of Cu⁺ and Cu²⁺. The breakthrough study was used to investigate the propylene adsorption of the prepared zeolites. Although the results showed that the zeolites selectively adsorbed propylene, which was contributed by the π -complex formation between the Cu⁺ and propylene, it was postulated in this work that there must be a certain exchange degree in the zeolites for the effects of the π -complexation to show any noticeable preferential adsorption towards propylene. The spent zeolites were regenerated and tested for their reusability. It was shown that there was a decrease in the adsorption capacities of the regenerated zeolites. In addition, Cu⁺ on the Cu(I)Y zeolite was less stable and more susceptible than that on the Cu(I)X zeolite.

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1. Introduction

Separation of light olefins and paraffins is an essential as both materials have many applications in petrochemical industry. Over 50% of light olefins (ethylene and propylene) are directly used as a monomer for polymerization. The remaining is used for other chemical production first and then converted to polymers and chemical solvents. The purity of olefin is a critical factor for the polymer production, which requires 99.5% or higher for polymer-grade propylene. Since the purity is an issue for production of light olefin, a suitable separation process is still needed for olefin and paraffin mixtures.

The cryogenic distillation has been widely used for petrochemical separation for many years. However, it needs a large number of trays is energy intensive. To minimise the energy consumption, adsorption, absorption, and membrane processes are used as an alternative. Among them, adsorption does not require high input energy to separate light olefins from paraffins because it separates by the interaction between an adsorbent and an adsorbate. The adsorption based process is normally applied into two modes of operations; pressure swing adsorption (PSA) and temperature swing adsorption (TSA) with typical adsorbents like carbons [1,2] and zeolites [3]. Moreover, the π -complexation formation between olefins and adsorbents is of interest because it is stronger than the van der Waal force. In essence, the π -complexation is a molecular interaction between olefin and a transition metal. Generally, Cu^+ and Ag^+ are effective metals that form π -bonding with olefins. However, this interaction is a weak chemical bond, which can be broken at moderate temperature and pressure.

The π -complexation begins with the Dewar-Catt-Duncanson model, which describes that the vacant s orbital of the metal received electron donation from the π orbital of the olefin. In addition, the back donation also occurs by the metal that donates electrons back from the d orbital

to the empty anti π -bonding orbital of the olefin. The illustration of Dewar-Catt-Duncanson model is shown in Figure 1.

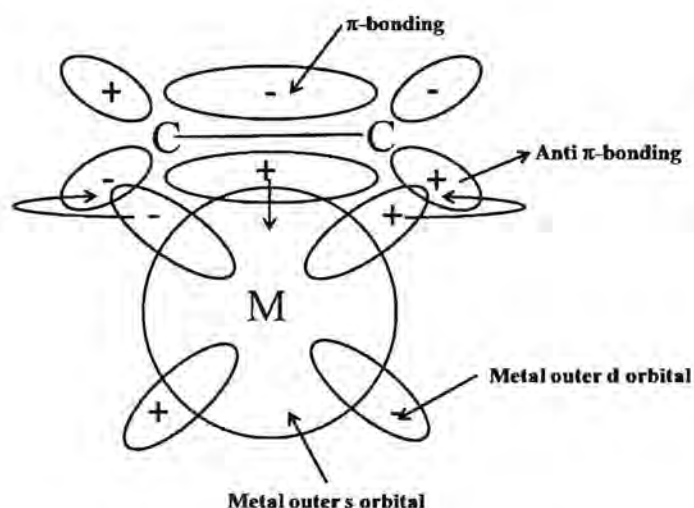


Figure 1 Dewar-Catt-Duncanson model of π -complexation [4]

There are some literature reporting roles of the π -complexation on the olefin/paraffin separation. Among the reported literature, a metal ions was introduced into the structure of zeolites by two different techniques, which are ion-exchange and monolayer dispersion method.

Wu et al. [5] prepared adsorbents modified with Ag^+ (Ag^+ -exchanged resins) for ethane/ethylene separation by adsorption. The results showed that ethylene selectivity and capacity were enhanced after the Ag^+ exchange. The modified adsorbent showed the potential for cyclic adsorption processes.

Takahashi and Yang [6] studied the purification of normal α olefins by removal of dienes using Ag^+ ion exchanged zeolite (Ag-Y) or $\text{AgNO}_3/\text{SiO}_2$ and Cu (I)-Y adsorbents. The results showed that the Cu^+ zeolite provided better diene/olefin separation than Ag-Y. Moreover, Cu-Y had higher H_2S and H_2 poisoning resistance.

Padin et al. [7] synthesized sorbents for olefin/paraffin separation by incipient wetness impregnation and ion exchange method. Ag^+ was dispersed on high-surface-area substrates and

exchanged into 5A zeolite and NaY in order to study roles of the π -complexation on the separation. The results indicated that the selectivity of butene/butane of monolayer $\text{AgNO}_3/\text{SiO}_2$ was 8.33 at 70°C and 1 atm. Moreover, the exchanged AgY zeolite had a potential for the purification of butene by removing small contents of butadiene.

Padin and Yang [8] studied the dispersion of Ag^+ cations on high-surface-area substrates, which are $\gamma\text{-Al}_2\text{O}_3$, SiO_2 and MCM-41 mesoporous molecular sieve for ethane/ethylene and propane/propylene separation. Two synthesis techniques, thermal monolayer dispersion and incipient wetness impregnation, were used. From the results, the incipient wetness impregnation technique yields the best sorbents that show the highest selectivities, olefin capacities, reversibility and fast adsorption rates. The silica surface (on both silica gel and MCM-41) provides a better substrate and consequently the Ag atoms in these sorbents are more capable of forming π -complexation with olefins.

Basaldella et al. [9] prepared mesoporous silica (SBA-15) under hydrothermal conditions with and without Cu cations by impregnation and investigated the adsorption behavior of propane/propylene in the presence and absence of this element. The results indicated that the adsorption uptake of propylene increased, while that for propane decreased in Cu/SBA-15 as compared with the SBA-15 sample. The presence of Cu atoms in the adsorbent lattice led to a greater selectivity towards propylene. Therefore, the Cu/SBA-15 sample can be recommended as an effective adsorbent for the PSA separation of propane/propylene mixtures at $110\text{-}135^\circ\text{C}$.

Van Miltenburg et al. [10] studied effective adsorbents for the ethylene/ethane separation by using the dispersions of CuCl in large NaX crystals. The results indicated that the maximum dispersion capacity of CuCl was 36 wt%. More importantly, CuCl/NaX preferred to adsorb the olefin because of the π -complexes of ethylene and CuCl.

Van Miltenburg et al. [11] investigated the adsorption of propylene and propane on NaX zeolite with and without the saturated dispersion of CuCl (36 wt %). Single component and binary

mixture adsorption was also observed. The results showed that the dispersion of CuCl improved the adsorption selectivity but reduced the adsorption capacity. NaX was more stable than CuCl/NaX during the exposure to the ambient atmosphere.

Grande et al [12] investigated the mesoporous silica (SBA-15) with and without silver-ion deposition for the separation of propane/propylene mixtures by adsorption via the π -complexation. The results indicated that the modified SBA-15 has better selectivity towards propylene than SBA-15.

Grande et al. [13] synthesized the mesoporous SBA-15 with Ag^+ deposition for propane/propylene adsorption. They varied two different silver loadings at Ag/SiO_2 equal to 0.5 and 1.0. The prepared adsorbents were preliminarily tested with vacuum-pressure swing adsorption units with a four-step cycle comprising feed. The results showed that the low silver content provided a better selectivity towards the olefin than the high silver loading. Propane leaving from the column had a very small concentration of propylene (less than 2%). At the blowdown step, propylene was obtained over 91%, which reached chemical grade propylene.

1.1 Objective

- 1.1.1 To synthesize Cu^+ on faujasites zeolites by ion exchange method with different reduction environments
- 1.1.2 To investigate effects of Cu^+ on faujasites zeolites on propane/propylene separation by breakthrough experiment

2. Methodology

2.1 Adsorbent Modification

NaX and NaY were used as an adsorbent. The ion exchange was used as the modification method. The adsorbent was exchanged with Cu^{2+} then reduced to Cu^+ . The modification procedures are as follows. NaX and NaY were used as received for exchanging with

ammonical copper solution in the ion exchange column at the room temperature by using a flow rate of 8 ml min^{-1} for 16 h. The ammonical copper solution was prepared by adding NH_4OH to a $0.015 \text{ M CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution. After that, the adsorbent was washed with deionized water and dried at room temperature overnight. Three different reduction environment were used to reduce Cu^{2+} to Cu^+ . The different reduction environments and a schematic of experimental setup for the zeolite preparation are shown in Table 1 and Figure 2, respectively.

2.2 Adsorbent Characterization

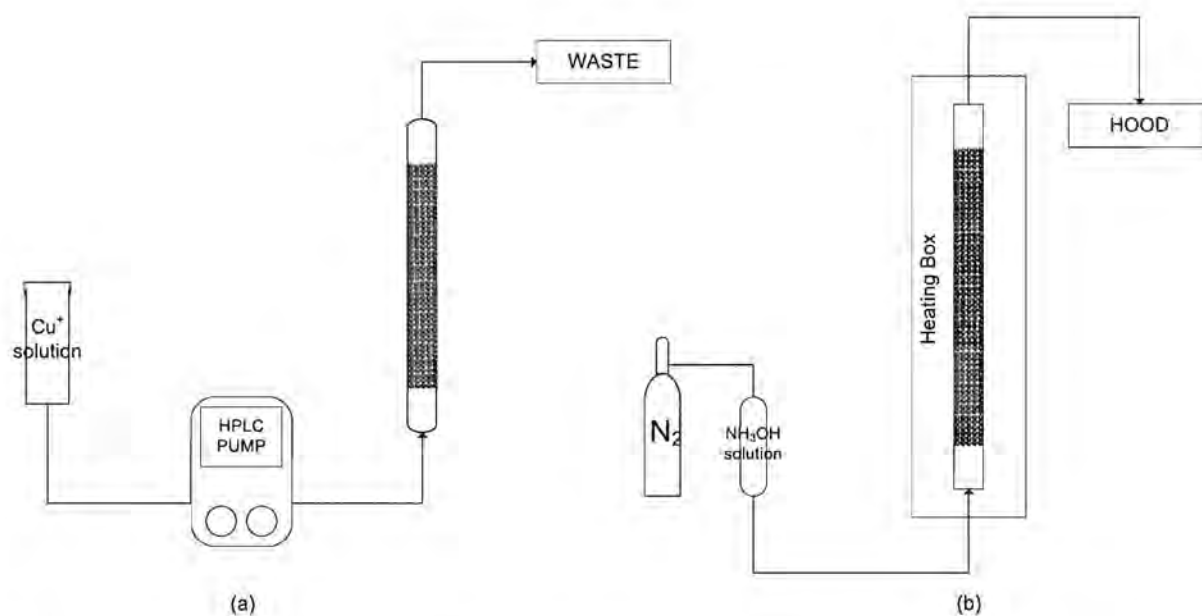
Modified adsorbents were characterized by X-ray photoelectron spectroscopy (XPS) in order to identify the oxidation states of copper in the modified adsorbent from different reduction environments. A PHI Quantera SKM, Scanning X-Ray Microprobe with $100 \mu\text{m}$, 100 W , $18 \text{ kV}/200 \mu\text{m}$ 40 W , and analyzed adsorbent area of $1.4 \text{ mm} \times 0.3 \text{ mm}$ per point for 2 h were the set conditions for the XPS analysis. The binding energy of C1s was used as a reference with an electron emission angle at 45° . The metal ion content was observed by inductively coupled plasma (ICP, PerkinElmer, Optima 3000DV).

2.3 Breakthrough Experiment

Breakthrough study was conducted at 30°C under atmospheric pressure in order to investigate the adsorption behavior of prepared adsorbents. Approximately, 47.0 g of an adsorbent was packed into a stainless steel column. The inlet gas of a 50:50 moles of propylene to propane was fed into the column with a flow rate of 50 ml min^{-1} . The effluent was collected and analyzed for propylene and propane composition by FTIR (Thermo, Nicolet 6700) every 15 sec. The spent adsorbent was regenerated with nitrogen at 150°C overnight after finishing the first adsorption. The breakthrough study was then repeated to investigate the stability and reusability of the adsorbent.

Table 1 Reduction environments used in this study.

Reagent	Temperature	Holding time	Further purged with only N ₂
NH ₄ OH/N ₂	room temperature to 350°C	1 h	1 h
NH ₄ OH/N ₂	room temperature to 350°C	2 h	1 h
H ₂	room temperature to 350°C	1 h	cooled down under N ₂ over night

**Figure 2** Experimental apparatus for the zeolite modification (a) ion-exchange step (b) reduction step.

3. Results and Discussion

Breakthrough profiles of propylene and propane from the beds of the Cu(I)X zeolite reduced with 1 h of ammonia, 2 h of ammonia, 1 h of hydrogen, and NaX zeolite are shown in Figure 3. The breakthrough times of the propylene and propane along with the calculated adsorbent capacities of propylene are in Table 2. It can be obviously seen that the breakthrough times of propylene are longer than that of propane for all tested zeolites indicating that the adsorbents selectively adsorb

propylene compared to propane.

Comparison between the three reduction methods shows that the Cu(I)X zeolite reduced with 1 h of hydrogen and reduced with 1 h of ammonia have slightly longer breakthrough times than that from the NaX zeolite, 148.0, 147.0, and 146.5 min, respectively. It indicates that the π -complex formation between Cu^+ in the X zeolite may not play a significant role to an extent that there is any different on the propylene/propane adsorption selectivity. Moreover, 1 h of hydrogen reduction results in a longer breakthrough time than the other reduction methods. This result shows that the hydrogen reduction is a better reduction method than the ammonia reduction.

However, increasing ammonia reduction time does not improve the propylene adsorption capacity. This results can be clearly seen by the shorter breakthrough of Cu(I)X zeolite reduced with 2 h of NH_4OH than that reduced with 1 h of NH_4OH , 124.5 and 147.0 min, respectively.

The XPS spectra and the binding energy at the $\text{Cu } 2\text{P}_{3/2}$ are shown in Figure 4 and Table 3, respectively. All XPS data were obtained from the Cu-exchanged with X zeolite reduced with three different reduction environments. The binding energy of the $\text{Cu } 2\text{P}_{3/2}$ in the Cu-exchanged X zeolite after reducing with 1 h (932.8 eV) and 2 h (932.6 eV) of ammonia and nitrogen is slightly higher than that of the Cu_2O reference (932.5 eV) indicating that the majority of the Cu-ion exists in the Cu^+ form with some in the Cu^{2+} form. For 1 h hydrogen reduction at 350°C , the zeolite has about 0.6 to 0.8 eV lower binding energy (932.0) than that of the other two reduction environments. This hardly indicates that this reduction method results in only Cu^{2+} because some area of the H_2 reduction peak overlaps with that of the Cu_2O reference. The XPS results indicate that the ammonia reduction gives a higher amount of Cu^+ in the Cu-exchange X zeolite than the hydrogen reduction. However, results from the breakthrough experiments show that the X zeolite reduced with the hydrogen reduction has higher propylene adsorption capacity than that with ammonia reduction. This implies that there may not be a direct correlation between the extent of Cu^+ presence in the zeolite and adsorption capacity of the olefin, but rather it affects the selectivity and breakthrough

time. Since, the Cu(I)X zeolite reduced with 1 h of hydrogen resulted in the highest propylene adsorption capacity, this reduction method was applied for Cu-exchange Y zeolite.

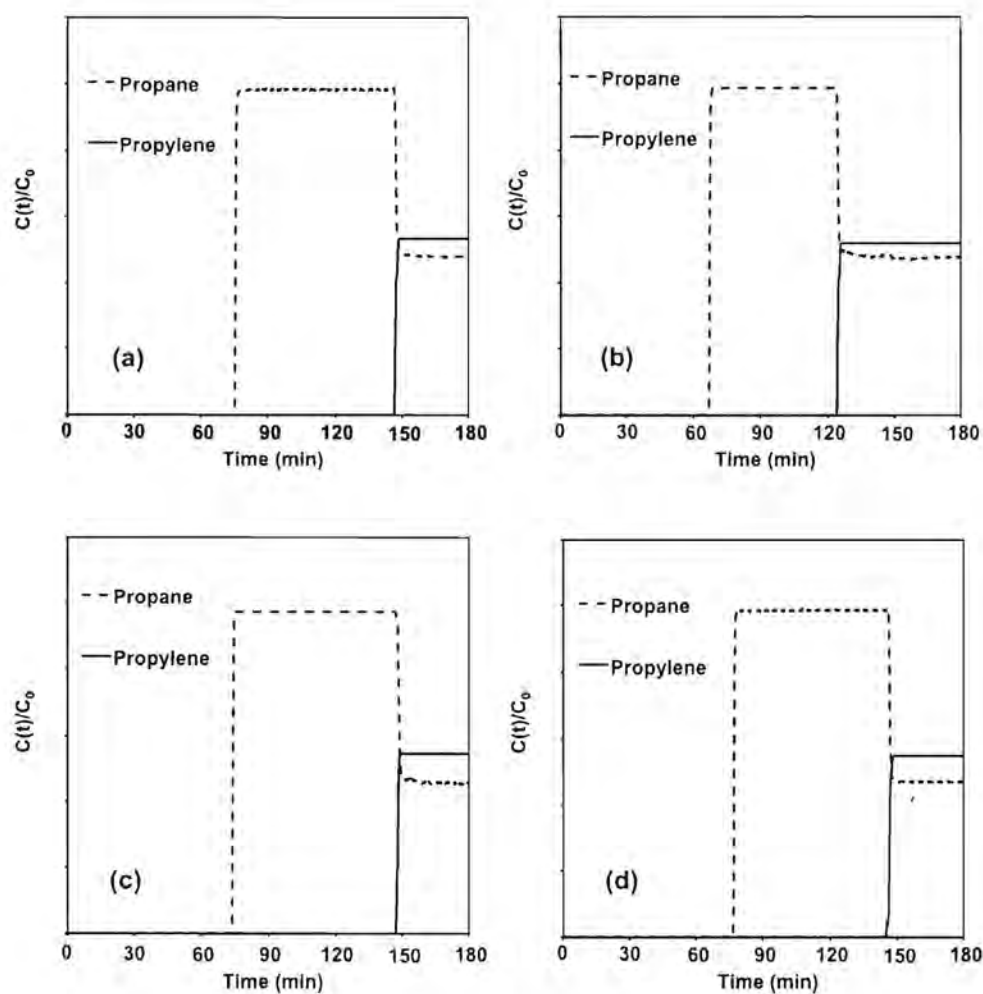


Figure 3. Breakthrough profiles of propylene and propane from (a) Cu(I)X zeolite with 1 h NH_4OH reduction, (b) Cu(I)X zeolite with 2 h NH_4OH reduction, (c) Cu(I)X zeolite with 1 h hydrogen reduction, and (d) NaX zeolite.

Table 2 Breakthrough times of propylene and propane and propylene adsorption capacities of Cu(I)X zeolite with 1 h NH₄OH reduction, Cu(I)X zeolite with 2 h NH₄OH reduction, Cu(I)X zeolite with 1 h hydrogen reduction, and NaX zeolite

	Cu(I)X reduced with 1 h NH ₄ OH	Cu(I)X reduced with 1 h NH ₄ OH	Cu(I)X reduced with 1 h H ₂	NaX
Propane breakthrough time (min)	75.0	67.0	74.5	77.0
Propylene breakthrough time (min)	147.0	124.5	148.0	146.5
Propylene adsorption (wt%)	12.4	9.3	13.2	12.7

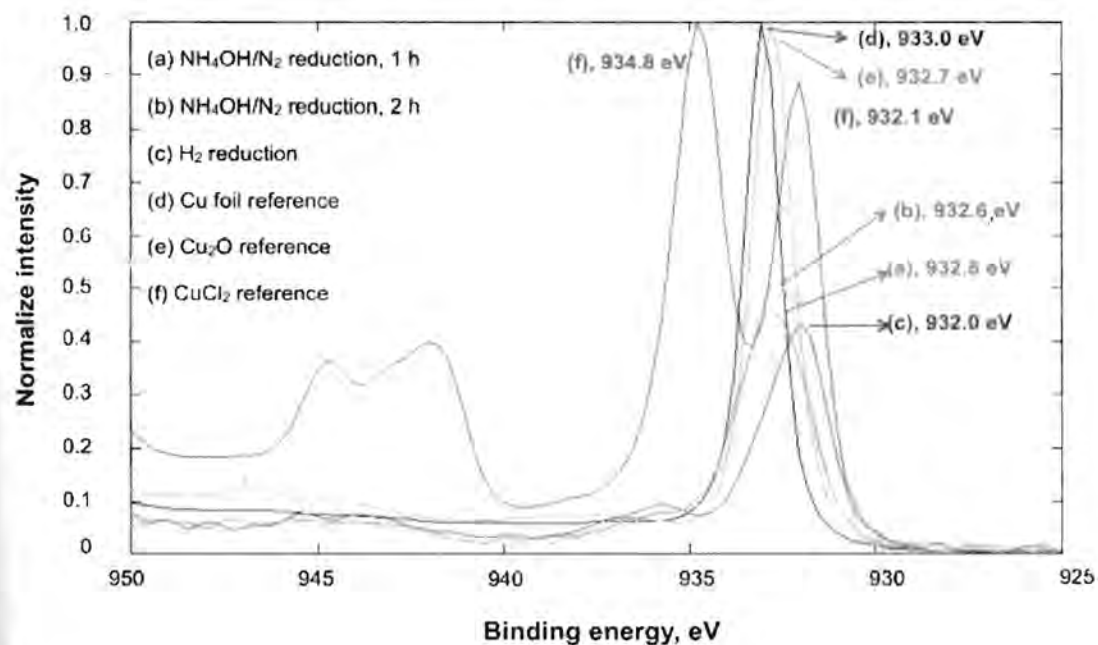


Figure 4. X-ray photoelectron spectroscopy (XPS) spectra of X zeolite subject to three reduction methods at Cu 2P_{3/2}.

Table 3 Binding energy of the X zeolite subject to the three reduction environments atCu $2P_{3/2}$.

Sample	Binding energy (eV)
NH ₄ OH/N ₂ at 350°C for 1 h	932.8
NH ₄ OH/N ₂ at 350°C for 2 h	932.6
H ₂ at 350°C for 1 h	932.0
Cu ₂ O reference	932.5
CuCl ₂ reference (14)	934.8
Cu foil reference	933.0

Breakthrough profiles of propylene and propane from Cu(I)Y zeolite reduced with 1 h of hydrogen, and NaY zeolite are shown in Figure 5. The breakthrough times of propylene and propane along with the calculated propylene adsorption capacity are also in Table 4. Comparison between Cu(I)Y and NaY zeolite, Cu(I)Y provide the longer breakthrough time than NaY zeolite, 146.0 and 128.5 min, respectively. This result implies that the effect of π -complexation between Cu⁺ in the Y zeolite and propylene are more pronounced. The calculated propylene adsorption capacity from the breakthrough profiles of Cu(I)Y is also higher than that of NaY zeolite. The propylene adsorption capacity of NaY and Cu(I)Y are 9.9 and 12.4 g /g zeolite, while those of NaX and Cu(I)X are 12.7 and 13.2 g/g zeolite, respectively. This result indicates that there are more effect of the π -complexation between Cu⁺ in the Y zeolite and propylene than that in the X zeolite. The different investigation on the X and Y zeolites can be explain by the different ion-exchange degrees on both zeolites. It can be postulated that there must be a certain exchange degree in the zeolites for the effects of the π -complexation to show any noticeable preferential adsorption towards propylene.

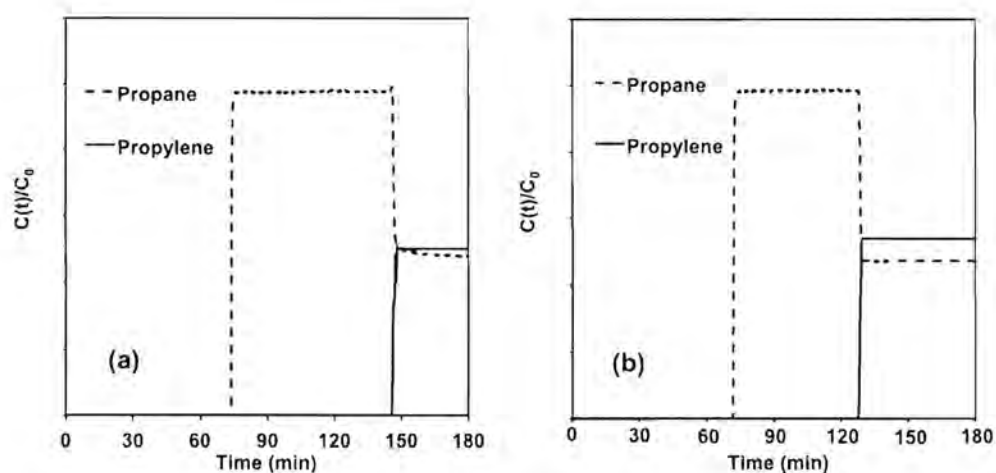


Figure 5. Breakthrough profiles of propylene and propane from (a) Cu(I)Y zeolite with 1 h H₂ reduction, and (b) NaY zeolite.

Table 4. Breakthrough times of propylene and propane and propylene adsorption capacity of Cu(I)Y zeolite with 1 h H₂ reduction, and NaY zeolite

	Cu(I)Y reduced with 1 h H₂	NaY
Propane breakthrough time (min)	74.0	72.0
Propylene breakthrough time (min)	146.0	128.5
Propylene adsorption (wt%)	12.4	9.9

Table 5. Metal contents in NaX, NaY, Cu(I)X reduced with 1 h of hydrogen, and Cu(I)Y reduced with 1 h of hydrogen

	Cu(I)X reduced with 1 h H₂	NaX	Cu(I)Y reduced with 1 h H₂	NaY
Si/Al	1.425	1.285	2.828	2.623
Cu/Al	0.588	-	0.725	-
Na/Al	0.295	1.000	0.225	1.000

The metal contents in NaX, NaY, Cu(I)X reduced with 1 h of hydrogen, and Cu(I)Y reduced with 1 h of hydrogen are shown in Table 5. The Cu(I)Y zeolite has a higher exchange degree than the Cu(I)X zeolite; therefore, the effects of the π -complexation of the former are clearly observed. Comparison between the Cu to Al ratio of the zeolites shows that the ratio of Cu(I)X (0.588) is lower than that of Cu(I)Y (0.725). In other words, the exchange degree of Cu^+ with Na^+ is lower in the X zeolite than the Y zeolite, even though the equivalent amount of Cu^+ in the ammoniacal copper solution (0.150 mol) is more than enough to provide complete ion exchange with Na^+ on the X zeolite (0.145 mole) and Y zeolite (0.096 mole). The incomplete ion exchange can be explained by the ammonia in $[\text{Cu}(\text{NH}_3)_4]^{2+}$, which is too large for the 6R pore opening of the zeolites, is not stripped from the solution shell at the normal exchange condition; hence, a lesser extent in the Cu^+ exchange with Na^+ . From the table 5, it can also be seen that the summation between the molar ratios of the Cu/Al and the Na/Al is lower than one. This is a results from the Cu-ion exists in the Cu^{2+} form instead of Cu^+ , and each Cu^{2+} compensates two aluminum sites.

Both Cu(I)X and Cu(I)Y were also regenerated with N_2 at 150°C overnight after finishing the first adsorption. The breakthrough profiles of propylene and propane from Cu(I)X zeolite and Cu(I)Y zeolite after regeneration are shown in Figure 6. Propylene and propane breakthrough times and adsorption capacities from the breakthrough profiles are compared to those from their fresh forms as shown in Table 6. The results show that there are significant decreases in the breakthrough times of propylene and propane from the regenerated zeolites compared to their fresh forms. However, the propylene breakthrough time from the regenerated Cu(I)X decreases about 27%, while that from the regenerated Cu(I)Y drops more than 50% from its original breakthrough time. In addition, the propylene adsorption capacity of the regenerated Cu(I)X decreases at a lower extent than that of the Cu(I)Y zeolite. This indicates that Cu^+ on the Cu(I)Y zeolite is less stable and more susceptible than that on the Cu(I)X zeolite.

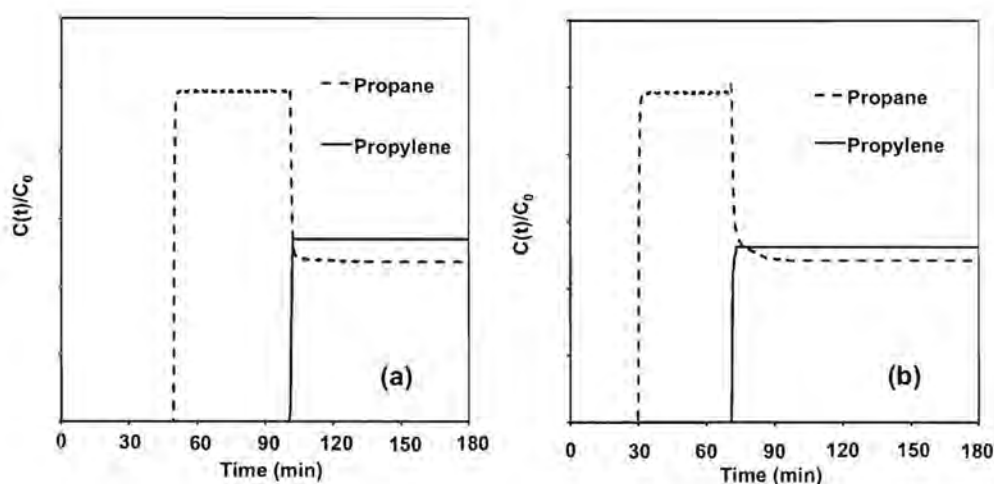


Figure 6 Breakthrough profiles of propylene and propane from (a) regenerated Cu(I)X and (b) regenerated Cu(I)Y.

Table 6. Breakthrough times of propylene and propane and propylene adsorption capacity of Cu(I)X zeolite, and Cu(I)Y zeolite after regenerated

	Cu(I)X after regenerated	Cu(I)X reduced with 1 h H₂	Cu(I)Y after regenerated	Cu(I)Y reduced with 1 h H₂
Propane breakthrough time (min)	49.5	74.5	30.0	74.0
Propylene breakthrough time (min)	101.0	148.0	71.5	146.0
Propylene adsorption (wt %)	8.8	13.2	6.6	12.4

4. Conclusions

Cu(I)X and Cu(I)Y zeolites were prepared from ion exchanging Na⁺ from NaX and NaY zeolites and subject to three different reduction environments. It was found that the 1 h hydrogen reduction resulted in the highest amount of propylene adsorption capacity of the prepared zeolites. Although the ion exchange method was proven to be successful in preparing Cu(I)X and Cu(I)Y,

there was a limitation on the incomplete ion exchange due mainly to the nature of chemical reactions of constituents in the solution for the exchange. For the propylene adsorption selectivity of the prepared zeolites, the breakthrough study showed that the π -complex between Cu^+ and propylene did contribute to the higher propylene adsorption capacity. It was also found that there were different propylene adsorption between the X and Y zeolites investigated in this work, which was postulated to be due to the difference in the ion-exchange degree in the zeolites. It seems that a certain exchange degree in the zeolites was required for the effects of the π -complexation to show any noticeable preferential adsorption towards propylene. There was a decrease in the propylene adsorption capacity of the regenerated prepared zeolites. Furthermore, stability of Cu^+ on the X and Y zeolites was different with Cu^+ in the latter reported to be less stable.

5. References

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Recommendations for future work

Further investigation on the separation in a larger scale would give valuable information to this work. In addition, consideration may be on the synthesis of zeolite with the copper ion other than using ion exchange to increase the amount of copper ion in the zeolite.