

CHAPTER IV

RESULTS AND DISCUSSION

This experiment studies hydrogen purification by adsorption. The factors that were studied are type of zeolite, temperature, bead size, initial pressure and the ratio of zeolite and alumina. The life time of the zeolite is also studied.

4.1 Characterization of adsorbents

The commercial adsorbents were used in this experiment are silica gel, activated alumina and 5 different type of zeolite (3A, 4A, 5A, 13X and beta). In order to verify types of zeolite, the XRD spectrum of each sample was compared with the reference patterns collected by International Zeolite Association Structure Commission (IZA-SC). XRD spectrum of zeolite samples were obtained using x-ray diffractometer (Rigaku D/MAX-2200 Ultima⁺). The XRD spectrum zeolite 3A, 4A, 4A (factory) 5A, beta and 13X exist in the respective sample (Figure 4.1 and 4.2) which correspondent to their structural units.

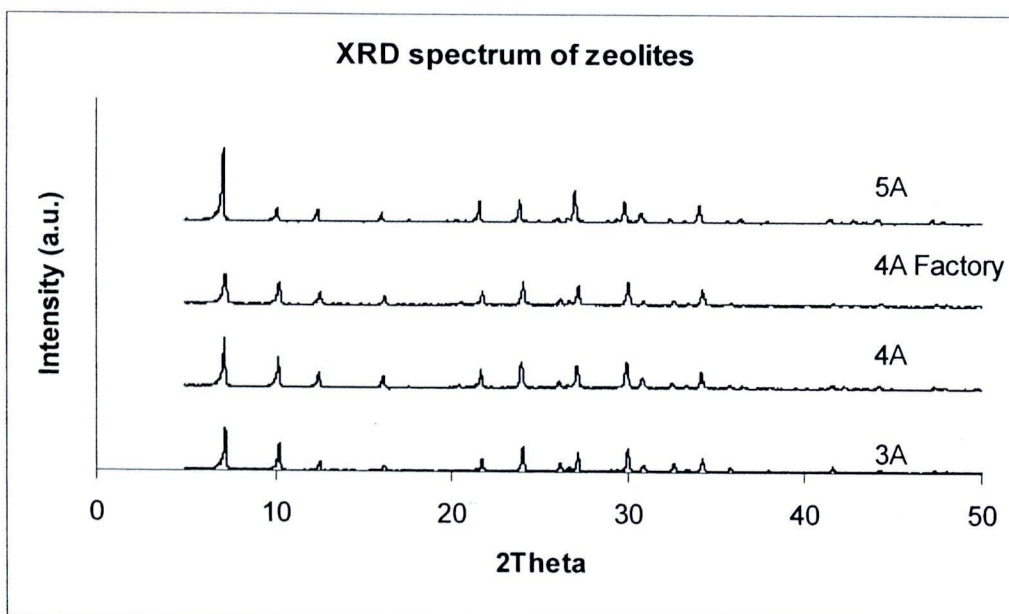


Figure 4.1 XRD spectrum of zeolite 3A, 4A, 4A factory, 5A.

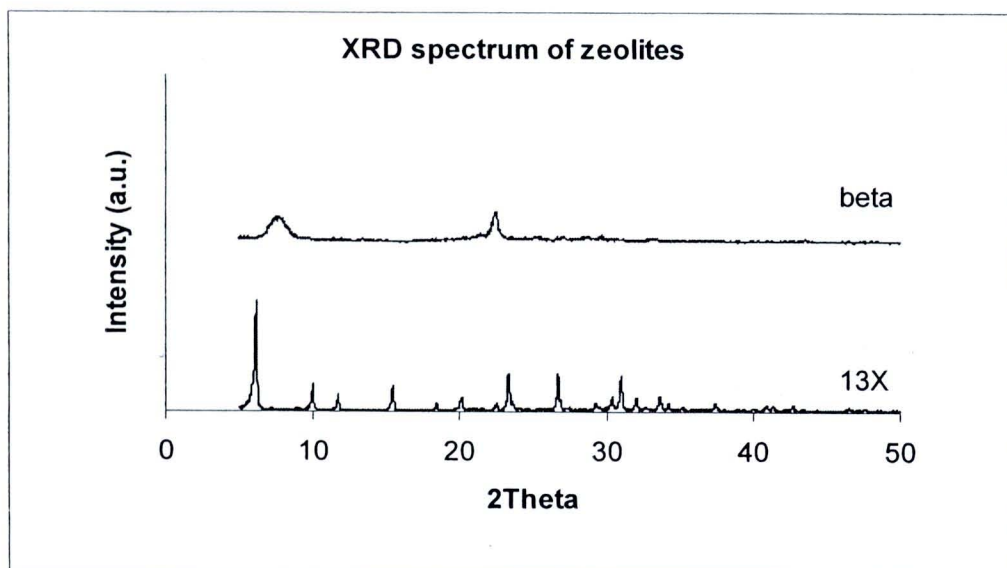


Figure 4.2 XRD spectrum of zeolite beta and 13X.

Surface area of zeolite 13X and beta was analyzed by BEL Japan, BELSORP-mini instrument. The samples were pre-treatment at 300°C for 3 hours. It is unable to analyze surface of zeolite 3A and 4A by this method because the pore size of these zeolites are too small to adsorb N₂. Surface area of zeolite 13X and beta are 531 and 681 (m²g⁻¹) respectively. N₂ adsorption-desorption isotherms of 13X and beta zeolite are showed in Figure 4.3.

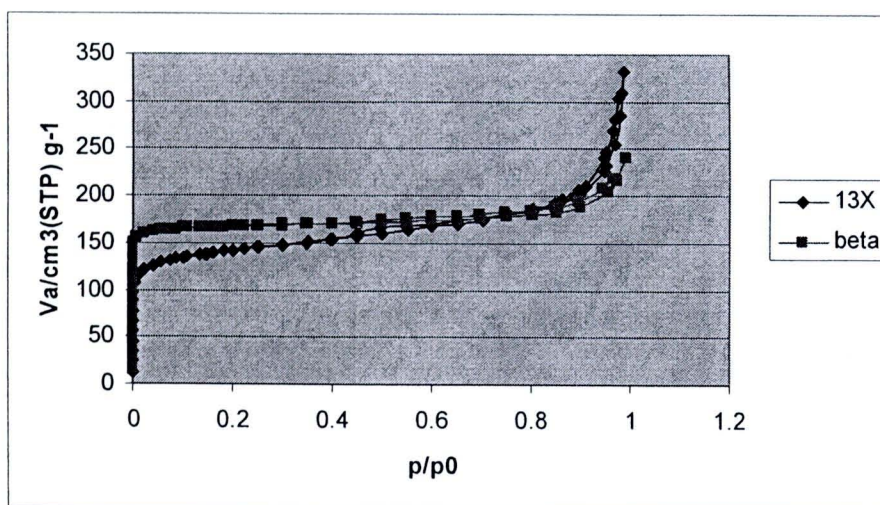


Figure 4.3 N₂ adsorption-desorption isotherms of 13X and beta zeolite.

4.2 Effect of molecular sieve (zeolite)

Effect of molecular sieve (zeolite) was determined by using the standard mixed gas (10.1% CO, 9.9% CO₂, 10.1% CH₄, 10.0% N₂, 59.8% H₂) flows through hydrogen purification system. The condition is shown as below. The obtained results are shown in the table 4.1.

| | | |
|----------------------------------|---|--------------------------|
| Feed gas | : | standard mixed gas |
| Zeolite | : | 3A, 4A, 5A, 13X and beta |
| Inlet pressure | : | 10 bar g |
| Temperature | : | -196°C |
| Pellet size | : | 2.5-5 mm. |
| Alumina : Zeolite : Alumina (g.) | : | 4.5 : 3 : 4.5 |

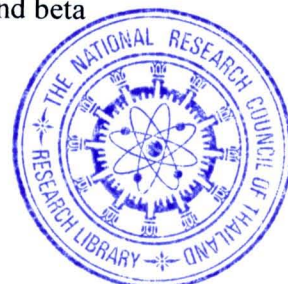


Table 4.1 Concentration of output gas (zeolite 3A, 4A, 5A, 13X, beta/-196°C/10 barg)

| Molecular sieve | Number run | H ₂ (%) | N ₂ (%) | CO (%) | CH ₄ (ppm) | CO ₂ (ppm) | Total |
|-----------------|-----------------|--------------------|--------------------|--------|-----------------------|-----------------------|-------|
| 3A | 1 st | 91.3 | 6.0 | 2.7 | 434 | 0 | 100 |
| | 2 nd | 91.3 | 5.9 | 2.8 | 461 | 1.1 | 100 |
| | avg | 91.3 | 6.0 | 2.8 | 448 | 0.6 | 100 |
| 4A | 1 st | 92.1 | 5.6 | 2.3 | 240 | 0 | 100 |
| | 2 nd | 91.2 | 5.9 | 2.9 | 460 | 0 | 100 |
| | avg | 91.7 | 5.8 | 2.6 | 350 | 0 | 100 |
| 5A | 1 st | 91.0 | 6.0 | 2.9 | 517 | 1.3 | 100 |
| | 2 nd | 91.1 | 6.0 | 2.9 | 533 | 0.3 | 100 |
| | avg | 91.1 | 6.0 | 2.9 | 525 | 0.8 | 100 |
| 13X | 1 st | 91.0 | 6.0 | 3.0 | 513 | 1.2 | 100 |
| | 2 nd | 90.9 | 6.1 | 3.0 | 509 | 1.0 | 100 |
| | avg | 91.0 | 6.1 | 3.0 | 511 | 1.1 | 100 |
| beta | 1 st | 93.5 | 4.6 | 1.7 | 278 | 0 | 100 |
| | 2 nd | 93.7 | 4.6 | 1.7 | 277 | 0 | 100 |
| | avg | 93.6 | 4.6 | 1.7 | 278 | 0 | 100 |

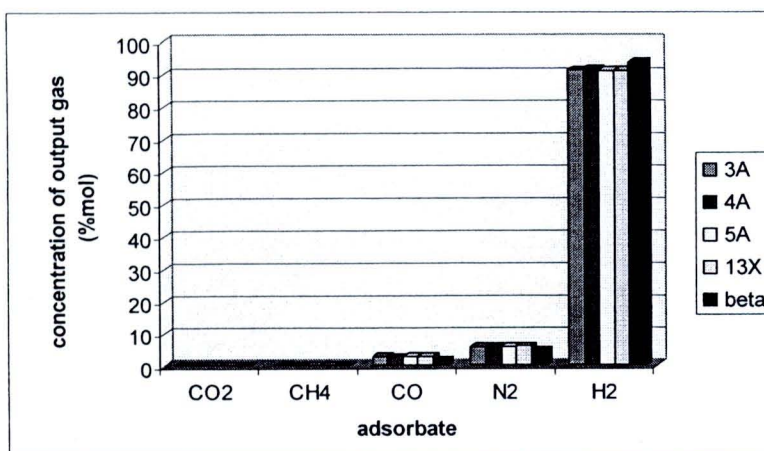


Figure 4.4 Concentration of output gas (zeolite 3A, 4A, 5A, 13X, beta/-196°C/10 barg).

Table 4.2 %Adsorption by zeolite 3A, 4A, 5A, 13X and beta (-196°C/10 barg)

| Molecular sieve | % Adsorption | | | |
|-----------------|----------------|------|-----------------|-----------------|
| | N ₂ | CO | CH ₄ | CO ₂ |
| 3A | 40.0 | 72.0 | 99.6% | 99.9% |
| 4A | 42.0 | 74.0 | 99.7% | 100% |
| 5A | 40.0 | 71.0 | 99.5% | 99.9% |
| 13X | 39.0 | 70.0 | 99.5% | 99.9% |
| beta | 54.0 | 83.0 | 99.7% | 100.0% |

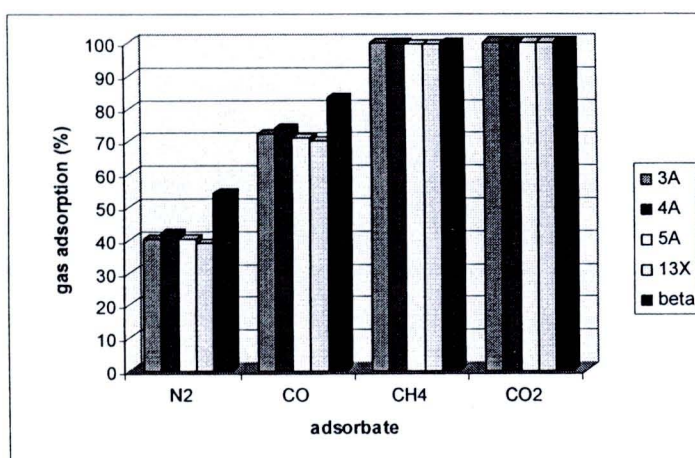


Figure 4.5 %Adsorption by zeolite 3A, 4A, 5A, 13X and beta (-196°C/10 barg).

Purity of hydrogen when using zeolite 3A, 4A, 5A, 13X and beta as adsorbent are 91.3, 91.7, 91.1, 91.0, 93.6% respectively, comparing to 59.8% of inlet standard mixed gas. CO₂ were adsorbed more than CH₄ > CO > N₂ in all type of zeolites. This result corresponds to Peiyuan Li which reported beta zeolite can adsorb CO₂ > CH₄ > N₂ > O₂ [8]. Gas adsorption ability of each zeolite from this experiment is shown below.

N₂ beta > 4A > 3A = 5A > 13X
 CO beta > 4A > 3A > 5A > 13X
 CH₄ beta > 4A > 3A > 13X > 5A
 CO₂ beta > 4A > 3A > 5A > 13X

Beta is a good adsorbent for all of gases. Refer to kinetic diameter theory CO, CO₂, CH₄, N₂ which has a kinetic diameter, σ of 3.76, 3.30, 3.80 and 3.64 Å respectively (Table 4.3). It seems appropriate to zeolite 4A which has a pore diameter of 4 Å. This is compared well to this experiment that adsorption ability of 4A for CO, CO₂, CH₄, N₂ is better than 3A, 5A and 13X. However, from this experiment beta zeolite which has pore diameter of 7.6×6.4 and 5.5×5.5 Å provides the best result for adsorption of CO, CO₂, CH₄, N₂. The result shows that not only pore diameter that affects the adsorption ability. The other factors are zeolite structure and adsorption area. The nitrogen adsorption analysis was done for zeolite beta and 13X. The results are 681 (m²g⁻¹) and 531 (m²g⁻¹) respectively which correspond to this experiment. The adsorption ability for N₂ of beta zeolite is better than zeolite 13X.

According to these results, Beta zeolite was chosen to be a representative for the next experiments.

Table 4.3 Dimensions of H₂, N₂, CO, CO₂, CH₄

| | Pauling | | Lennard-Jones | |
|-----------------|------------|-----------|------------------|---------------------------|
| | length (Å) | Width (Å) | γ min (Å) | σ (Å) ^a |
| H ₂ | 3.1 | 2.4 | 3.24 | 2.89 |
| N ₂ | 4.1 | 3 | 4.09 | 3.64 |
| CO | 4.2 | 3.7 | 4.25 | 3.76 |
| CO ₂ | 5.1 | 3.7 | | 3.30 |
| CH ₄ | | 4.2 | 4.25 | 3.80 |

^a Kinetic diameter, σ calculated from the minimum equilibrium cross-sectional diameter.

4.3 Effect of the temperature

Effect of temperature was determined by using the following conditions. The results are shown in the table 4.4.

| | | |
|----------------------------------|---|-----------------------------|
| Feed gas | : | standard mixed gas |
| Zeolite | : | Beta |
| Initial pressure | : | 10 barg |
| Temperature | : | -196°C, 0°C, ambient (25°C) |
| Pellet size | : | 2.5-5 mm. |
| Alumina : Zeolite : Alumina (g.) | : | 4.5 : 3 : 4.5 |

Table 4.4 Concentration of output gas (beta zeolite/-196°C, 0°C, ambient/10 barg)

| Molecular sieve | Number run | H ₂ (%) | N ₂ (%) | CO (%) | CH ₄ (%) | CO ₂ (%) | Total |
|-----------------|-----------------|--------------------|--------------------|--------|---------------------|---------------------|-------|
| Beta -196°C | 1 st | 93.5 | 4.6 | 1.7 | 277 ppm | 0 | 100 |
| | 2 nd | 93.7 | 4.6 | 1.7 | 277 ppm | 0 | 100 |
| | avg | 93.6 | 4.6 | 1.7 | 277 ppm | 0 | 100 |
| Beta 0°C | 1 st | 62.6 | 10.4 | 10.3 | 10.4 | 6.6 | 100 |
| | 2 nd | 62.0 | 10.3 | 10.1 | 10.1 | 7.3 | 100 |
| | avg | 62.3 | 10.4 | 10.2 | 10.3 | 7.0 | 100 |
| Beta ambient | 1 st | 61.4 | 10.2 | 10.1 | 10.3 | 7.9 | 100 |
| | 2 nd | 61.7 | 10.2 | 10.2 | 10.3 | 7.6 | 100 |
| | avg | 61.6 | 10.2 | 10.2 | 10.3 | 7.8 | 100 |

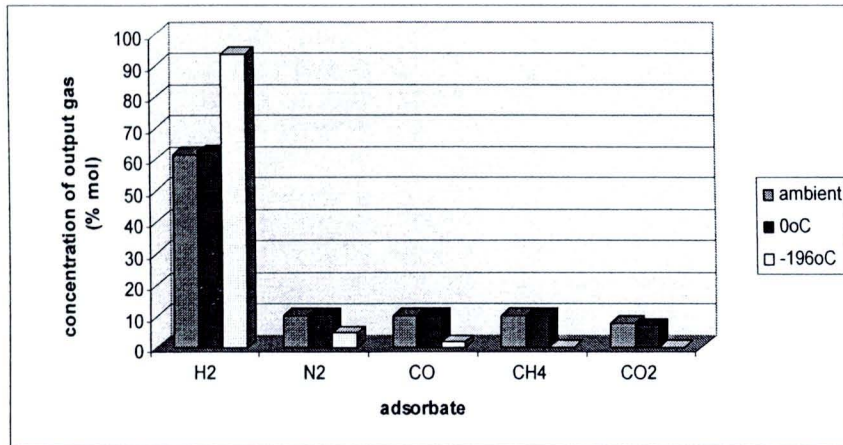


Figure 4.6 Concentration of output gas (beta zeolite/-196°C, 0°C, ambient/10 barg).

The purity of hydrogen when using beta zeolite at -196°C, 0°C, ambient are 93.6%, 62.3%, 61.6% respectively. The result at -196°C is obviously better than at 0°C and ambient. Beta zeolite does not adsorb N₂, CO, CH₄ at 0°C and ambient, only CO₂ will be adsorbed. The purity of hydrogen at 0°C are better than at ambient (25°C). This can be concluded that decreasing the temperature of the gas-solid system at a constant pressure will increase the quantity of x adsorbed.

$$X = f(t)_p$$

This is because gas molecules, upon collision with cooled surfaces, lose a significant amount of their thermal energy to the cooled surface. In general it may be said that the thermal energy of a gas molecule is determined almost entirely by the temperature of the last surface where the gas molecule desorbed from. If a surface is intentionally cooled to the temperature of liquid nitrogen (-196°C or 77K), all gas molecules which have a boiling point higher than -196°C can be cryo-condensed on this surface. These gas molecules will literally freeze, transforming from a gas to a solid. As solid material, these condensed gases are capture [15]. Table 4.5 shows boiling and melting point of CO, CO₂, CH₄, N₂ and H₂ respectively. At -196°C, solid property of CO₂ is more than CH₄ and liquid property of CO is more than N₂ which correspond to the results that CO₂ can be adsorped more than CH₄ > CO > N₂. According to the result

decreasing the temperature will increase gas adsorption. This corresponds to Vithitsan's experiment which reported that adsorption of moisture on zeolite 3A at 90°C is better than 110°C [11] and Peiyuan Li which reported that with beta zeolite, the kinetic separation factors are very small at high temperatures for all system studied (CH_4/N_2 , CH_4/O_2 , N_2/O_2 , N_2/CO_2 , O_2/CO_2) [8].

Table 4.5 boiling and melting point of CO, CO₂, CH₄, N₂ and H₂

| Gas type | Boiling point (°C) | Melting point (°C) | State at -196°C |
|-----------------|--------------------|--------------------|-----------------|
| CO | -192 | -205 | liquid |
| CO ₂ | -78 | -57 | solid |
| CH ₄ | -161.6 | -185.5 | solid |
| N ₂ | -195.79 | -210 | liquid |
| H ₂ | -252.87 | -259.14 | gas |

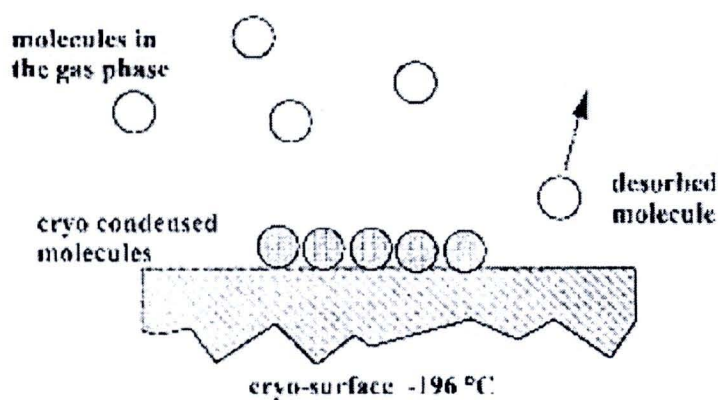


Figure 4.7 Molecules in the gas phase, upon contact with a liquid nitrogen temperature surface, condense on that surface. The residence time for molecules is dependent upon the species of gas, the temperature of the cryo-surface and the heat of adsorption.

From the temperature study, the temperature of -196°C was chosen for the next experiments.

4.4 Effect of the inlet pressure

Effect of the initial pressure was determined by using the following conditions.

The results are shown in the table 4.6.

| | | |
|----------------------------------|---|--------------------|
| Feed gas | : | standard mixed gas |
| Zeolite | : | Beta |
| Inlet pressure | : | 5, 10, 15, 20 barg |
| Temperature | : | -196°C |
| Pellet size | : | 2.5-5 mm. |
| Alumina : Zeolite : Alumina (g.) | : | 4.5 : 3 : 4.5 |

Table 4.6 Concentration of output gas (beta zeolite/-196°C/5, 10, 15, 20 barg)

| Molecular sieve | Number run | H ₂ (%) | N ₂ (%) | CO (%) | CH ₄ (ppm) | CO ₂ (ppm) | Total |
|-----------------|-----------------|--------------------|--------------------|--------|-----------------------|-----------------------|-------|
| 5 barg | 1 st | 94.3 | 4.3 | 1.4 | 258 | 0.4 | 100 |
| | 2 nd | 93.2 | 4.7 | 1.7 | 282 | 0.6 | 100 |
| | avg | 93.8 | 4.5 | 1.6 | 270 | 0.5 | 100 |
| 10 barg | 1 st | 93.5 | 4.6 | 1.7 | 278 | 0 | 100 |
| | 2 nd | 93.7 | 4.6 | 1.7 | 277 | 0 | 100 |
| | avg | 93.6 | 4.6 | 1.7 | 278 | 0 | 100 |
| 15barg | 1 st | 91.3 | 6.0 | 2.7 | 439 | 1.3 | 100 |
| | 2 nd | 90.9 | 6.2 | 2.8 | 528 | 1.0 | 100 |
| | avg | 91.1 | 6.1 | 2.8 | 484 | 1.2 | 100 |
| 20barg | 1 st | 89.8 | 6.9 | 3.3 | 627 | 1.0 | 100 |
| | 2 nd | 91.3 | 6.0 | 2.7 | 467 | 1.6 | 100 |
| | avg | 90.6 | 6.5 | 3.0 | 547 | 1.3 | 100 |

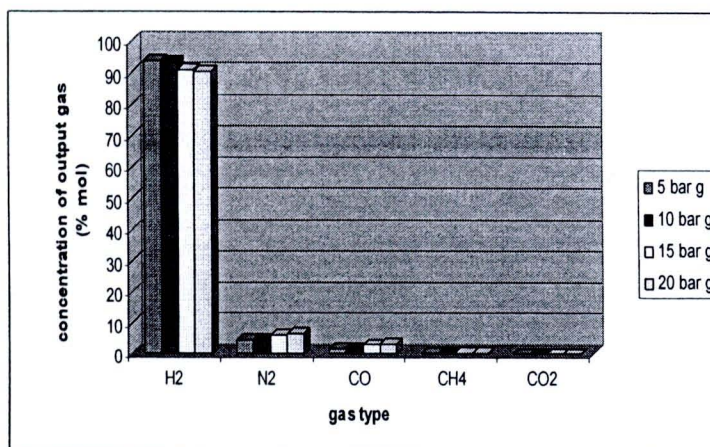


Figure 4.8 Concentration of output gas (beta zeolite/-196°C/ 5, 10, 15, 20 barg).

Purity of hydrogen will be increased when decreasing the inlet pressure. The purity of hydrogen at 5, 10, 15, 20 barg are 93.8, 93.6, 90.9, 90.6% respectively. This is explained by the adsorption time. At low pressure, the flow rate is also low. Therefore, there is much time for adsorption. This corresponds to Vithitsan's experiment which reported that adsorption of moisture on zeolite 3A at 1 mL/min. is better than 2 mL/min [11].

The adsorption pressure can be fixed by either available feed pressure or the required product pressure. Although a high feed gas pressure is always preferred for high hydrogen recovery and low investment costs but the purity of hydrogen is decreased.

In this experiment, the purity of hydrogen at 5 and 10 barg are not much different. To increase the productivity, pressure 10 barg was chosen for the next experiments.

4.5 Effect of the pellet size

In order to utilize the adsorption characteristics of zeolites in separation processes, commercial molecular sieve adsorbents are prepared as pelleted agglomerates containing a high percentage of the crystalline zeolite together with the necessary amount of an inert binder. The effect of pellet size was studied by using the 2.5-5 mm. and 1-2 mm. of zeolite 3A. The condition is below. The results are shown in the table 4.7.

| | | |
|----------|---|--------------------|
| Feed gas | : | standard mixed gas |
| Zeolite | : | 3A |

Initial pressure : 10 barg
 Temperature : -196°C
 Pellet size : 2.5-5 mm., 1-2 mm.
 Alumina : Zeolite : Alumina (g.) : 4.5 : 3 : 4.5

Table 4.7 Concentration of output gas (2.5 mm.,1-2 mm. of zeolite 3A/-196°C/10 barg)

| Molecular Sieve | # run | H ₂ (%) | N ₂ (%) | CO (%) | CH ₄ (ppm) | CO ₂ (ppm) | Total |
|---------------------|-----------------|--------------------|--------------------|--------|-----------------------|-----------------------|-------|
| Beta (2.5-5 mm.) | 1 st | 93.5 | 4.6 | 1.7 | 278 | 0 | 100 |
| | 2 nd | 93.7 | 4.6 | 1.7 | 277 | 0 | 100 |
| | avg | 93.6 | 4.6 | 1.7 | 278 | 0 | 100 |
| 3A (2.5-5 mm) | 1 st | 91.3 | 6.0 | 2.7 | 434 | 0 | 100 |
| | 2 nd | 91.3 | 5.9 | 2.8 | 461 | 1.1 | 100 |
| | avg | 91.3 | 6.0 | 2.8 | 448 | 0.6 | 100 |
| 3A (1-2 mm) | 1 st | 91.0 | 6.0 | 2.9 | 511 | 0.4 | 100 |
| | 2 nd | 90.9 | 7.2 | 1.8 | 557 | 1.8 | 100 |
| | avg | 91.0 | 6.6 | 2.4 | 534 | 1.1 | 100 |

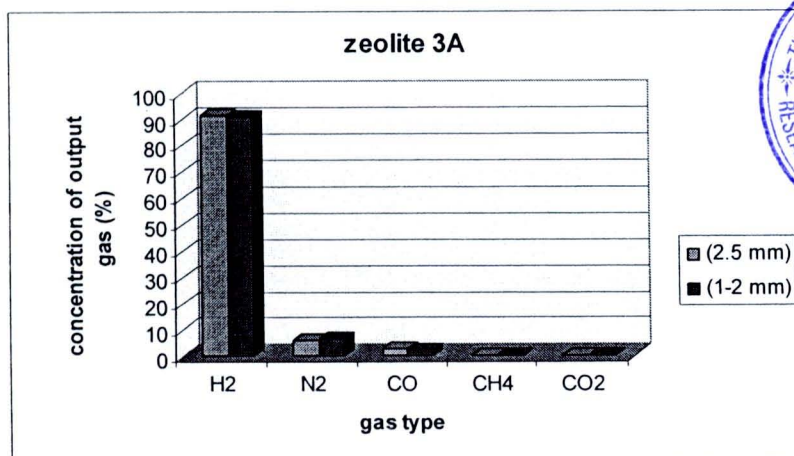


Figure 4.9 Concentration of output gas (2.5 mm.,1-2 mm. of zeolite 3A/-196°C/10 barg).

Purity of hydrogen when use 2.5-5 mm. and 1-2 mm. of zeolite 3A, -196°C are 91.3% and 91.0% respectively. The results are not much different. This is because adsorption is a matter of pore filling. The external surface area which takes a few percent of the total area doesn't play an important role in adsorption for this case.

4.6 Effect of ratio between alumina and zeolite

In this experiment alumina and zeolites were used to adsorb gas impurities of hydrogen. Effect of ratio between alumina and zeolite was studied. The condition is following. The results are shown in the table 4.8.

| | | |
|------------------------------|---|------------------------|
| Feed gas | : | standard mixed gas |
| Zeolite type | : | 3A, beta |
| Inlet pressure | : | 10 barg |
| Temperature | : | -196°C |
| Pellet size | : | 2.5 mm. |
| Adsorbent ratio | | |
| Alumina:Zeolite:Alumina (g.) | : | 0 : 12 : 0 |
| | : | 6 : 0 : 6 |
| | : | 4.5 : 3 : 4.5 |
| | : | 2.5 : 7 : 2.5 |

Table 4.8 Concentration of output gas by vary ratio of alumina and zeolite.

| Molecular sieve | Ratio(alumina: zeolite:alumina) (g) | # run | H ₂ (%) | N ₂ (%) | CO (%) | CH ₄ (ppm) | CO ₂ (ppm) | Total |
|-----------------|-------------------------------------|-----------------|--------------------|--------------------|--------|-----------------------|-----------------------|-------|
| Beta | (0:12:0) | 1 st | 93.7 | 4.4 | 1.8 | 422 | 0 | 100 |
| | | 2 nd | 94.5 | 3.8 | 1.6 | 441 | 0 | 100 |
| | | avg | 94.1 | 4.1 | 1.7 | 432 | 0 | 100 |
| 3A | (0:12:0) | 1 st | 87.7 | 7.2 | 4.7 | 1361 | 0 | 100 |
| | | 2 nd | 87.8 | 7.3 | 4.7 | 1377 | 0 | 100 |
| | | avg | 87.8 | 7.3 | 4.7 | 1369 | 0 | 100 |
| Alumina | (6:0:6) | 1 st | 92.0 | 5.7 | 2.4 | 370 | 0.1 | 100 |
| | | 2 nd | 92.1 | 5.4 | 2.4 | 322 | 0.1 | 100 |
| | | avg | 92.1 | 5.6 | 2.4 | 346 | 0.1 | 100 |

| Molecular sieve | Ratio (alumina: zeolite: alumina) (g.) | # run | H ₂ (%) | N ₂ (%) | CO (%) | CH ₄ (ppm) | CO ₂ (ppm) | Total |
|-----------------|--|-----------------|--------------------|--------------------|--------|-----------------------|-----------------------|-------|
| beta | (4.5:3:4.5) | 1 st | 93.5 | 4.6 | 1.7 | 278 | 0 | 100 |
| | | 2 nd | 93.7 | 4.6 | 1.7 | 277 | 0 | 100 |
| | | avg | 93.6 | 4.6 | 1.7 | 278 | 0 | 100 |
| | (2.5:7:2.5) | 1 st | 93.5 | 4.7 | 1.7 | 380 | 0 | 100 |
| | | 2 nd | 93.5 | 4.8 | 1.7 | 292 | 0 | 100 |
| | | avg | 93.5 | 4.8 | 1.7 | 336 | 0 | 100 |
| 3A | (4.5:3:4.5) | 1 st | 91.3 | 6.0 | 2.7 | 434 | 0 | 100 |
| | | 2 nd | 91.3 | 5.9 | 2.8 | 461 | 1.1 | 100 |
| | | avg | 91.3 | 6.0 | 2.8 | 448 | 0.6 | 100 |
| | (2.5:7:2.5) | 1 st | 89.9 | 6.5 | 3.6 | 691 | 0 | 100 |
| | | 2 nd | 89.8 | 6.4 | 3.7 | 746 | 1 | 100 |
| | | avg | 89.9 | 6.5 | 3.7 | 719 | 0.5 | 100 |

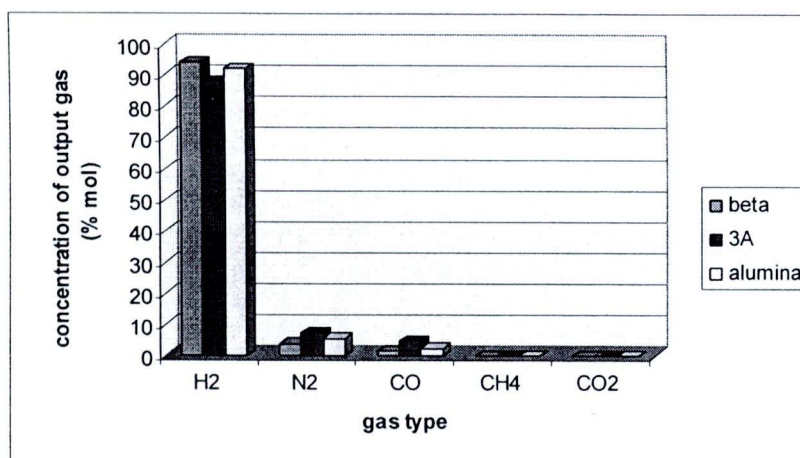


Figure 4.10 Concentration of output gas (zeolite 3A, beta, alumina (12g.)/-196°C/10 barg.).

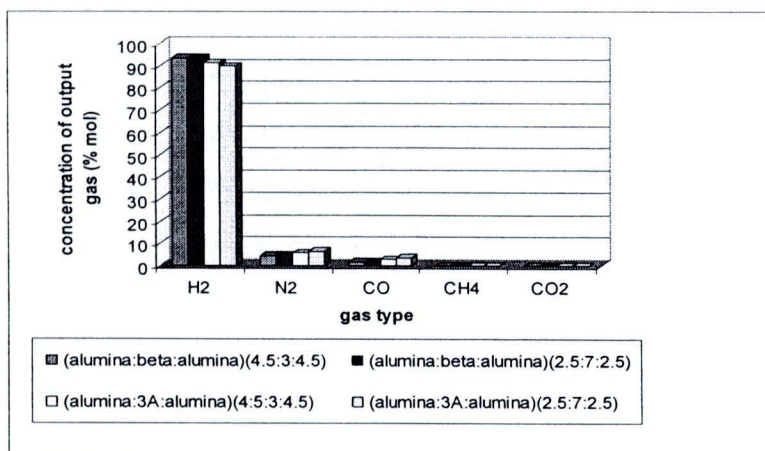


Figure 4.11 Concentration of output gas (zeolite 3A, beta/alumina:zeolite; 9:3, 5:7/-196°C/10 barg).

Purity of hydrogen when use 100% of zeolite beta, 3A and alumina are 94.1, 87.8, 92.1 respectively. The adsorption ability of zeolites and alumina are shown below.

| | |
|-----------------|---------------------|
| N ₂ | beta > alumina > 3A |
| CO | beta > alumina > 3A |
| CH ₄ | alumina > beta > 3A |
| CO ₂ | beta = 3A > alumina |

Alumina can adsorb CH₄ well, when beta can adsorb N₂, CO and CO₂ well. Increasing the alumina content would make CH₄ adsorption much better. This result corresponds to mixing alumina and zeolite adsorbent. At higher alumina content adsorbent, it exhibits lower CH₄ content of outlet gas in both cases of beta and 3A zeolites. However the most appropriate ratio is 4.5 : 3 : 4.5 of alumina : zeolite : alumina which makes the hydrogen purity to be 93.6% in case of beta zeolite is an adsorbent.

Activated alumina does not possess an ordered crystal structure and consequently the pores are nonuniform. The distribution of the pore diameters within the adsorbent particles may be narrow (20 to 50 Å) or it may range widely (20 to several thousand Å). Hence, all molecular species, with the possible exception of high molecular weight polymeric materials, may enter the pores. The major use of activated alumina as a sorbent

is in drying. The moisture content can be reduced to below 1 ppm using activated alumina in suitable designed adsorbers.

Zeolite molecular sieves have pores of uniform size (3Å to 10Å) which are uniquely determined by the unit structure of the crystal. These pores will completely exclude molecules which are larger than their diameter [6].

4.7 Life time of adsorbents

All adsorption systems are cyclic in nature i.e. there is an adsorption cycle followed by regeneration cycle, which enables repeated use of adsorbent. In this experiment, the thermal was employed for regeneration and the stability period of the zeolite was studied. Four times of calcination (300°C for zeolite beta and 180°C for alumina, 3 hours) are done and hydrogen purification are repeated by using the following condition. The results are in the table 4.9 and figure 4.12.

| | | |
|-----------------------------------|---|--------------------|
| Feed gas | : | standard mixed gas |
| Zeolite | : | beta |
| Initial pressure | : | 10 barg |
| Temperature | : | -196°C |
| Pellet size | : | 2.5-5 mm. |
| Alumina : Zeolite : Alumina (wt): | | 4.5 : 3 : 4.5 |

Table 4.9 Concentration of output gas after each calcination (beta zeolite/-196°C/10 barg).

| | # run | H ₂ (%) | N ₂ (%) | CO (%) | CH ₄ (ppm) | CO ₂ (ppm) | Total |
|-----------------|-----------------|--------------------|--------------------|--------|-----------------------|-----------------------|-------|
| Calcination 1st | 1 st | 93.5 | 4.6 | 1.7 | 278 | 0 | 100 |
| | 2 nd | 93.7 | 4.6 | 1.7 | 277 | 0 | 100 |
| | avg | 93.6 | 4.6 | 1.7 | 278 | 0 | 100 |
| Calcination 2nd | 1 st | 91.9 | 5.5 | 2.5 | 319 | 0.1 | 100 |
| | 2 nd | 91.6 | 5.6 | 2.8 | 422 | 0 | 100 |
| | 3 rd | 92.8 | 5.0 | 2.2 | 322 | 0 | 100 |
| | avg | 92.1 | 5.4 | 2.5 | 354 | 0.05 | 100 |
| Calcination 3rd | 1 st | 92.8 | 5.0 | 2.1 | 262 | 0 | 100 |
| | 2 nd | 91.9 | 5.4 | 2.6 | 326 | 0.07 | 100 |
| | avg | 92.4 | 5.2 | 2.4 | 294 | 0.04 | 100 |
| Calcination 4th | 1 st | 92.7 | 5.2 | 2.1 | 264 | 0 | 100 |
| | 2 nd | 92.3 | 5.4 | 2.3 | 332 | 0 | 100 |
| | avg | 92.5 | 5.3 | 2.2 | 298 | 0.00 | 100 |

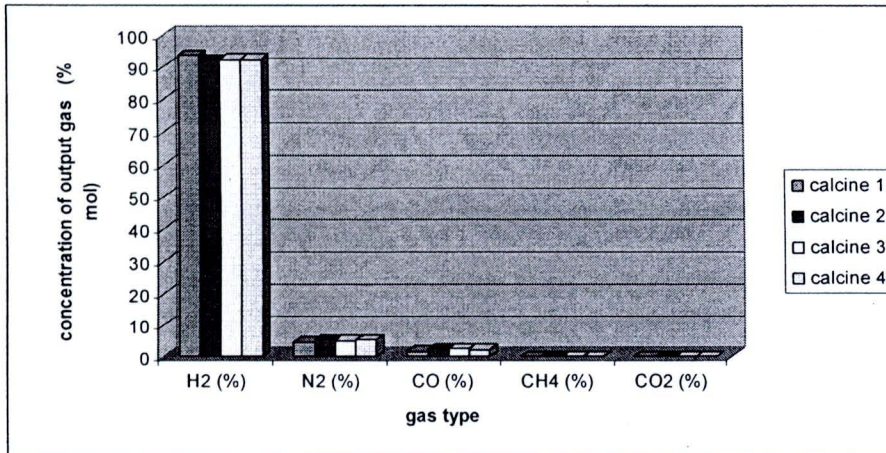


Figure 4.12 Concentration of output gas after each calcination (beta zeolite/-196°C/10barg).

Hydrogen concentration of output gas after 1st, 2nd, 3rd, 4th calcinations is 93.6, 92.1, 92.4, 92.5 respectively. The concentration of hydrogen after the second time of regeneration is less than the first one around 1.6%. The concentration of hydrogen after the 2nd, 3rd, 4th of regeneration is not much different. This result corresponds to the Shang-Bin Liu's experiment which reported that the structure of beta zeolite is a small destruction at 400°C [12].

4.8 Comparison the best and present condition.

The present and the best condition are compared by using standard mix gas and hydrogen (industrial grade) as an inlet gas. The condition is below. The results are in the table 4.10.

| | Best condition | Factory condition |
|------------------------------|-----------------------------------|--------------------------|
| Feed gas | : standard mixed gas | |
| | : H ₂ industrial grade | |
| Zeolite | : beta | 4A (Factory) |
| Inlet pressure | : 10 barg | 15 barg |
| Temperature | : -196°C | -196°C |
| Pellet size | : 2.5-5 mm. | 2.5-5 mm. |
| Alumina:Zeolite:Alumina (g.) | : 4.5:3:4.5 | 4.5 : 3 : 4.5 |



Table 4.10 Compare concentration of output gas by present factory condition and best condition.

| Feed Gas | Condition | # run | H₂ (%) | N₂ (%) | CO (%) | CH₄ (ppm) | CO₂ (ppm) | Total | |
|--|----------------------|-----------------|--------------------------------|--------------------------------|---------------------|---------------------------------|---------------------------------|---------------------------|---|
| Standard Mixed Gas | Factory Condition | 1 st | 90.3 | 6.6 | 3.1 | 482 | 0.9 | 100 | |
| | | 2 nd | 90.3 | 6.4 | 3.3 | 641 | 0.6 | 100 | |
| | | avg | 90.3 | 6.5 | 3.2 | 562 | 0.8 | 100 | |
| | Best Condition | 1 st | 93.5 | 4.6 | 1.7 | 278 | 0 | 100 | |
| | | 2 nd | 93.7 | 4.6 | 1.7 | 277 | 0 | 100 | |
| | | avg | 93.6 | 4.6 | 1.7 | 278 | 0 | 100 | |
| Feed Gas | Condition | # run | O₂ (ppm) | N₂ (ppm) | CO (ppm) | CH₄ (ppm) | CO₂ (ppm) | Impurity (ppm) | H₂ purity (%) |
| H ₂ Ind. | | | 5.8259 | 1.7145 | 2.3011 | 0 | 1.2459 | 9.8415 | 99.9990 |
| H ₂ Industrial Grade (99.8%) | Factory Condition | 1 st | 2.0341 | 0.5369 | 1.5297 | 0 | 0 | 4.1007 | 99.9996 |
| | | 2 nd | 2.0886 | 0.6152 | 1.7105 | 0 | 0 | 4.4143 | 99.9996 |
| | | avg | 2.0614 | 0.5761 | 1.6201 | 0 | 0 | 4.2576 | 99.9996 |
| | Best Condition | 1 st | 0.7716 | 0.3019 | 0.2913 | 0 | 0 | 1.3648 | 99.9999 |
| | | 2 nd | 1.3346 | 0.1957 | 0.2894 | 0 | 0 | 1.8197 | 99.9998 |
| | | avg | 1.0531 | 0.2488 | 0.2903 | 0 | 0 | 1.5922 | 99.9999 |

Table 4.11 Product specification of hydrogen

| Gas | Typical Level | Production Specification | Selling Specification |
|------------------------------------|--|---|---|
| Hydrogen, industrial grade (99.8%) | Purity 99.8%min O ₂ < 200 ppm H ₂ O < 200 ppm N ₂ < 1000 ppm | Purity 99.8%min O ₂ < 200 ppm H ₂ O < 200 ppm | Purity 99.8% min |
| Hydrogen, UHP (99.999%) | Purity 99.999%min. O ₂ < 2 ppm H ₂ O < 3 ppm THC as CH ₄ < 1 ppm N ₂ < 4ppm CO < 0.5ppm CO ₂ < 1ppm | Purity 99.999%min O ₂ < 2 ppm H ₂ O < 3 ppm THC as CH ₄ < 1 ppm | Purity 99.999%min O ₂ < 2 ppm H ₂ O < 3 ppm THC as CH ₄ < 1 ppm |

source : Thai Industrial Gases (Public) Co.,Ltd.

The hydrogen concentration of output gas after using standard mixed gas as a feed gas with the present factory condition and our best condition are 90.3% and 93.3% respectively. When hydrogen industrial grade was used as a feed gas with the present and our best condition, the hydrogen concentration are 99.9996 and 99.9999% respectively. The purity of hydrogen after using our best condition is better than the specification. Especially, O₂ and CO levels are lower than maximum limit of UHP H₂ gas specification. This beta zeolite adsorbent exhibits the superior property than the present factory condition. Therefore, it can be concluded that the suitable zeolite for hydrogen purification by absorption process is beta zeolite. The inlet pressure is 10 barg and the temperature is -196°C. The pellet size is 2.5-5 mm. and the ratio of alumina:zeolite:alumina is 4.5:3:4.5. By this condition hydrogen purity would increase up to 99.9999%. This would raise the product quality and make it is valuable.