Study On The Mechanism of CO₂ Adsorption Process on zeolite 5A as a Molecular Sieve In RDE System: An Infrared Investigation

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Abstract. BATAN has a plan to build an Experimental Power Reactor which is called RDE. RDE10 is designed based on HTGR technology. The main safety systems applied in the RDE are inherent safety. One of the systems in the RDE is the helium purification system. The helium purification system has a function to maintain the helium quality of the experimental power plant cooling in accordance with requirements. The problem in RDE system is there some the impurity gas into reactor coolant occurs because of water ingress and air ingress. One of impurities that may exist in the RDE system is the presence of CO2. The presence of impurities in the coolant will threaten the material integrity of the system structures and reactor components thus disrupting the safety and reliability of the operation. Therefore a done the study of the process of the mechanism of absorption of co2 by zeolite 5A as molecular sieve and its investigation using FTIR. The results of the study obtained information that the process of absorption of CO2 into zeolite 5A occurs by physisorption and chemisorption. The molecule will bind to the zeolite surface with the van der waals bond. And by chemisorption, the oxygen in CO2 will bind to Al on the zeolite by forming a covalent bond. The adsorption mechanism in zeolite 5A can be done by using FTIR with functional group analysis.

Keywords: CO2, Adsorption molecular sieve, 5A zeolite

1. Introduction
National Nuclear Energy Agency of Indonesia (BATAN) has been given the task to conduct a national program to develop and construct a pebble bed type high temperature reactor called Reaktor Daya Eksperimental (RDE)[1]. RDE is designed based on HTGR technology [2]. The main safety system applied in the RDE is inherent safety. This safety system on the reactor has negative reactivity coefficient to the temperature rise, thus ensuring the reactor core operating temperature does not exceed 1,600 °C. Graphite is a major component in the reactor core system since graphite has a melting point of 2,300 °C, guaranteed not to be damaged / melted in the event of an helium reactor coolant loss accident [3]. Water ingress and air ingress occurring in the reactor under normal operating condition or under transient condition will cause aggressive impurities in the reactor coolant. The
presence of impurities in the coolant will threaten the material integrity of the system structures and reactor components thus disrupting the safety and reliability of the operation [4]. To avoid oxidation of graphite and corrosion of reactor structural materials, helium purification system as an indispensable auxiliary system of RDE is set up to eliminate various gaseous impurities entering primary circuit coolant to limited levels. These impurities include chemical components such as hydrogen, water vapor, oxygen, carbon monoxide, carbon dioxide, methane and nitrogen as well as radionuclide fission products such as krypton and xenon etc. Impurities occur due to the water and air interaction with the graphite inside the core[5-6]. Some steps must be conducted in helium purification system such as separating carbon dust particles using cartridge filter, the oxidation of the impurity, water condensation and molecular adsorption using molecular sieve, zeolite A5[1,5]. The absorption of CO, CO$_2$ and CH$_4$ gas is very important in the helium gas purification system in RDE. The impurities must be eliminated using purification of helium gas [7].

Figure 1. Helium Purification System (HPS) has the main function to maintain the quality of helium cooling in accordance with the requirements[8]

The method using in this work is reviewing several papers of CO$_2$ adsorption by zeolite as a molecular sieve. Therefore, the purpose of this paper is to provide information about the mechanism of CO$_2$ adsorption process in molecular sieve and to provide the information about infrared spectroscopy analysis that can be used to investigate the process of adsorption of CO$_2$ on the molecular sieve.

2. Methodology
The method using in this work is to review the several researchs that have been done, especially about the role of FTIR in investigating on process of CO$_2$ absorption using zeolite 5A.

3. Results and Discussion
3.1. Molecular Sieve
In helium purification system of RDE, the molecular sieve adsorber is the largest among the three fixedbed mentioned ahead due to relatively higher impurity concentration and lower adsorption capacity of carbon dioxide as well as smaller bulk density of the adsorbent. Consequently, the adsorption capacity of carbon dioxide on 5A is crucial for process and ultimately decides the size of
helium purification system of RDE. The partial pressure of carbon dioxide in primary circuit of RDE is about tens Pa. There are many works focus on \( \text{CO}_2 \) adsorption on molecular sieves, typically for carbon dioxide capture to control the greenhouse gas [9]. However, the comprehensive adsorption data of carbon dioxide on 5A at low partial pressure range serving for the design of helium purification system have been rarely available in open literature.

Molecular sieve is intended to absorb the gas impurity, like as carbon dioxide. One candidate of materials that can be used as molecular sieve is zeolite. Zeolite has been reported as a significant material in the application of catalysis, absorption, and ion-exchanging due to their microporous structure. The most commonly used zeolite is Faujasite (FAU) type adsorbents whereby the framework is composed of \( \text{AlO}_4 \) and \( \text{SiO}_4 \) tetrahedron like as figure 2.

![Figure 2. Center occupied by Al\(^{3+}\) or Si\(^{4+}\) atom with four O atom at the corners](image)

It can also be viewed as \( \text{SiO}_2 \) with some \( \text{SiO}_4 \) tetrahedron substituted by \( \text{AlO}_4 \), resulting in electronegativity of the framework. It can be balanced by the cations attaching to the framework in the pores, such as Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), NH\(^{4+}\), etc. These cations are always easy to be exchanged with external ions. The number and sites of the cations strongly affect the properties of the zeolites. In the some framework, silicon atoms are replaced with aluminum atoms, which are only coordinated with 3 oxygen atoms. The aluminum atoms only have an atom charge 3+, while silicon has atom charge 4+. The existence of this aluminum atom will cause the molecular sieve to have an atom negative charge. This atom negative charge causes the molecular sieve to bind the cation, in this case the impurity of helium gas [10,11].

According to their molecular sieve properties, zeolites act as selective regenerable adsorbents for purification of gaseous streams and separation of vapors and gases. In this respect, the so-called type A zeolites, denoted with the International Zeolite Association (IZA) code Linde Type A (LTA) [12]. There are large industrial application for drying of technical gases and liquids and for the n/i-alkane separation in discontinuous sorption processes [13].

The calcium exchanged form, Ca-LTA (5A zeolite), finds wide application for \( \text{CO}_2 \) and \( \text{CH}_4 \) adsorption from several gas mixture such as air [14,15]. Zeolite 5A could be selective for \( \text{CO}_2 \) and \( \text{CH}_4 \) adsorption due to the strong interactions of the quadruple moment of \( \text{CO}_2 \), \( \text{CH}_4 \) and the cation positioned in the zeolite structure [16]. Zeolite 5A as molecular sieve has properties as follows: [17,18].

| Properties                  | Zeolite 5A                          |
|-----------------------------|-------------------------------------|
| Chemical formula            | \( \text{Ca}_3\text{Na}_5\text{(AlO}_2\text{)}_{12}\text{(SiO}_2\text{)}_{12}.x\text{H}_2\text{O} \) |
| Size (mm)                   | 1/16 inch (1.46–1.97x1~6)           |
| Bulk density (kg/m\(^3\))   | 670                                 |
| BET surface area (m\(^2\)/gr)| 463                                 |
| Nominal micropore diameter (Å)| 5                                   |

This zeolite 5A has unique selectivity, acid properties and high thermal stability, uniform pore size, definite skeleton structure, and high porosity.
3.2. Mechanism of CO\textsubscript{2} Adsorption on zeolite 5A

Adsorption is usually described through isotherms, that is, the equal amount between adsorbate and the adsorbent as a function of its pressure for gas or concentration for liquid at constant temperature. Mechanism of CO\textsubscript{2} adsorption follows the physical adsorption and chemical adsorption.

Physisorption, shown schematically in Figure 5, the target molecules are attracted to the surface of pore walls within a high surface-area sorbent by van der Waals forces and have a low heat of adsorption that is only slightly greater than heat of sublimation of the adsorbate. This type is suitable for the insoluble adsorption process in the adsorbent but only to the surface only. Surface leave by adsorbat can be replaced by other adsorbat (multilayer). In the CO\textsubscript{2} adsorption can be occured by chemical adsorption if a chemical reaction occurs at the exposed surface or by physical adsorption [19]. In physisorption the CO\textsubscript{2} is adsorbed weakly by the substrate itself, in chemisorption, the CO\textsubscript{2} is adsorbed more strongly by specific binding sites.

![Figure 3. Promising CO\textsubscript{2} sorbents for physisorption on zeolite 5A][20]

Chemisorption, it is a process involving the exchange and transfer of valence electrons between the molecule adsorbent and atoms (molecules) on the surface of the adsorbent to form a covalent bond. This process will decrease the adsorbent capacity due to its strong covalent bind so that the process is not reversible. The bond is formed strongly which is a monolayer[21][22].

![Figure 4. Physisorption phenomenon and chemisorption phenomenon, bonding occurs between molecules and absorption][21]

![Figure 5. Chemisorption CO\textsubscript{2} on zeolite][22]
3.3. Effect of temperature and pressure on adsorption capacity

The higher temperature will decrease the absorption in molecular sieve. The molecular motion kinetics of the gas becomes more dynamic, cause it is difficult to catch gas into the molecular sieve porosity. After impurity gas is captured in the porosity of the molecular sieve surface, the gas will be easily released again [23-25].

The higher pressure applied to the system cause the greater the amount of CO$_2$ absorbed. At higher pressure these gases will be forced to enter into the pores of the Molecular Sieve through the PSA (Pressure Swing Adsorption) phenomenon. When the pressure applied to the molecular sieve column increases, the amount of captured impurities is also greater [26].

CO$_2$ adsorption on zeolite 5A will occur on physisorption and chemisorption. This is evidenced by the research Adam Hughmanick Berger has done research on comparing physisorption and chemisorption solid sorbents use to separate CO$_2$ from gas using temperature swing adsorption, that temperature and pressure greatly affect the process of adsorption of CO$_2$ by zeolite A5[27]. Sorbents with small heats of adsorption will require a much larger change in temperature to affect the same change in adsorbed capacity as a sorbent with a large heat of adsorption would experience from a small temperature swing. The Langmuir model is a reasonable assumption for both chemisorption and physisorption. In the chemisorption, there are a fixed number of Al-O sites, each of which will bind to the carbon dioxide. In physisorption, the fixed number of sites is equivalent to the monolayer coating of carbon dioxide that would correspond to a saturated sorbent. Figure 8 shows the correlation between temperature and pressure on CO$_2$ adsorption process by zeolite A5.

**Figure 6.** Adsorption of CO$_2$ by zeolite A5 on temperature variation and variation of partial pressure following Langmuir isotherms [27]

CO$_2$ adsorption will decrease if temperature rises. This can be explained by the fact that increasing temperature definitely enhances the diffusion of carbon dioxide from the gas bulk flow to the surface of the adsorbent. The smaller the mass-transfer resistance for the diffusion of carbon dioxide, the less the difference between the equilibrium adsorption capacity and kinetic adsorption capacity at breakthrough point.

3.4. Investigation of CO$_2$ adsorption on zeolite 5A

The adsorption process of CO$_2$ by zeolite 5A can be analyzed with FTIR measurements. From some experiments of CO$_2$ adsorption process by zeolite 5A there will be some spectra indicating CO$_2$ already adsorbed among others spectra in 3600-3400 cm$^{-1}$, spectra 1700-1600 cm$^{-1}$, spectra 1400-1300 cm$^{-1}$, spectra 1100- 900 cm$^{-1}$, as well as on the fingerprint area. This is as it is done on tania research[11]
The analysis using infrared spectroscopy will be obtained that information shows quite strong bands of hydroxyl groups at 3555 and 3514 cm\(^{-1}\). The component at 3514 cm\(^{-1}\) is assigned to Si(OH)Al as zeolite protonic centers that bridging OH groups. While the component at 3555 cm\(^{-1}\) is assigned to residual Ca(OH\(^{+}\))\[^{28}\]. Band at 1450 and 1435 cm\(^{-1}\) is evident, symmetric carbonate ions (CO\(_2\) asymmetric stretching). Band at 1120 cm\(^{-1}\) is Si-O-Al asymmetric stretching. There is a transmission windows below 751 cm\(^{-1}\). The band from 900-400 cm\(^{-1}\) appears to be aromatic C-H group out of bending vibration. FTIR spectrum from this region can be divided into four sub peak. The sub peaks include four adjacent aromatic C-H bonds at approximately 450 cm\(^{-1}\) and 550 cm\(^{-1}\), two adjacent aromatic C-H bonds at approximately (700–750) cm\(^{-1}\). CO\(_2\) adsorption can detect on symmetrical band, centered at 2351 cm\(^{-1}\). The position of this band is slightly shifted upwards with respect to the position of the asymmetric O-C-O stretching of CO\(_2\) [29-32]. CO\(_2\) adsorption on Ca-zeolite (5A-zeolite) provided evidence for the formation of CO\(_2\) bonded single Ca\(^{2+}\) ion and of two CO\(_2\) molecules over a single Ca\(^{2+}\) ion seem to be formed. Complex interactions, involving the coordination of CO\(_2\) with two cations were also characterized on other alkali-exchanged zeolite [33]. In the measurement result using FTIR on CO\(_2\) adsorption process on zeolite 5A is found that CO\(_2\) will be bound to zeolite 5A by forming CaCO\(_2\) bond[28].

**Table 2. Peak assignment of CO\(_2\) adsorption on zeolite 5A**

| Assignment                                      | Center (cm\(^{-1}\)) |
|------------------------------------------------|-----------------------|
| Aromatic bonds, (C-H) out of plane bending.     | 700-900               |
| Alkyl ethers, Si-O                              | 1008                  |
| Alkyl ethers, Si-O                              | 1060                  |
| \(\nu\) C-O, sec. alcohols                     | 1120                  |
| \(\nu\) C-O, tert.alcohols, ethers             | 1435                  |
| C-O                                            | 1450                  |
| Aromatic C=C                                    | 3514                  |
| OH                                              | 3555                  |

4. **Conclusion**

A study has been conducted on the adsorption mechanism of CO\(_2\) in zeolite 5A and its investigation using FTIR. From the study, it was found that CO\(_2\) would be absorbed into zeolite 5A in physisorption and chemisorption. The pressure and temperature will affect with the CO\(_2\) adsorption process in
zeolite 5A. Temperature and pressure are greater applied to the system, the CO$_2$ adsorption process on zeolite 5A is smaller. FTIR is one of the tools that can be used to detect CO$_2$ adsorption process in zeolite 5A with functional group analysis.

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