Role of TiO$_2$ pillared bentonite-Co catalyst Ni to convert glucose hydrogenation to be sorbitol

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Abstract. Glucose hydrogenation using water at solvent was happened trough two step. First, water was reduced to hydrogen and an oxygen gases by TiO$_2$ pillared bentonite. Second, hydrogen that produced was used to reduce glucose into sorbitol. The reaction was prepared in transparent medium for 30 days along under UV from sunlight. The product of reaction was characterized using FTIR and $^1$H-NMR spectroscopy.

1. Introduction

Clay mineral is one of Indonesia’s abundant natural resources and has not been used optimally. Clays geologically is a natural mineral from the family of crystalline silicates with a layered structure (Kama, 2002). Bentonite is a type of clay that is widely available in Indonesia which there are in most areas of Nusa Tenggara, Sulawesi, West Java, Central Java, Yogyakarata, East Java, South Sumatra, Jambi, North Sumatra [1].

Bentonite has a strong capability of colloids, when mixed with water it can expand. The surface and pore bentonite may convert the pores metal become wider. Another method to expand the pores is pillaring method. In this case, bentonite pores containing Na and K metal intercalated with metals of larger diameter so that the pores expands, then calcined at a temperature of 300-500°C, the metals will form an oxide layer bonded to produce bentonite pillared. In North Sumatra there are two types natural bentonite, wyoming bentonite and non Wyoming bentonite, and both have the main composition of SiO$_2$ / Al$_2$O$_3$ with (4-6 : 1) ratio. Bentonite is the common name of a type of clay that can be used to adsorb color, oils, fats and waxes. Pale land is a silicate of a variety of compositions, the main constituent of SiO$_2$ and Al$_2$O$_3$ containing water and chemically bonded. In addition to the above two compounds bentonite also contains CaO, MgO, Fe$_2$O$_3$, Na$_2$O and K$_2$O. Based on the theory of Davis and Masser that differences in levels of SiO$_2$ and Al$_2$O$_3$ ratio will affect the active power. Soil that has a big ratio of SiO$_2$ and Al$_2$O$_3$ is best soils adsorb. While land with a small ratio of SiO$_2$ and Al$_2$O$_3$ have the small ability to absorb. Comparison of SiO$_2$ and Al$_2$O$_3$ for a good bentonite is 5-6: 1, which is able to absorb, and has a large surface area.

Bentonite has a strong capability of colloids, when mixed with water, it can inflate (Wyoming). Bentonite in the dry state beige to green with a specific gravity of 2.4 to 2.8 g / mm$^3$ and a melting point between 1330-1430°C. Natural bentonite generally contain little calcite, carbonate, gypsum and quartz. Surface and pores natural bentonite can be enlarged with the activation of chemical and physical techniques [2], or by using pillaring elements Zr, Ti, Fe, Na, Ca through intercalation technique and calcinations at 450°C to produce pillared bentonite called photocatalyst powder [3,4].
Semiconductor photo catalyst powder has been widely studied, found that the activity of the photocatalyst is getting better with decreasing particle size causes increased surface area. A decrease in particle size between 5-10 nm causes changes in energy band structure of the semiconductor becomes known as a side effect Quantum. Further research has been done to produce photochemical of various sizes and shapes, particles of semiconductor chologenide such as CdS, ZnS, CdSe, GeSe, ZnSe and oxide semiconductors of the type ZnO, Fe₂O₃, TiO₂ has been widely used to photocatalysts for producing hydrogen from water [5].

Principle alter the surface and pore bentonite is by dissolving the metals contained in the pores of bentonite with an acid and metal is already late because the pores become wider. Another method to expand the pores by means pillaring, in this case pores bentonite containing Na and K metal intercalated with metal cations diameter is larger so that the pores inflates, then calcined at a temperature of 300-500° C [6, 7]. The metals will form oxides bonded to inter-layers, resulting pillared bentonite [8]. Through this technique would be great porosity bentonite, metal oxides as pillaring agent can be used for the catalyst.

In this research, intercalation bentonite pores using TiO₂ and calcination temperatures of 300-500° C to produce TiO₂ - pillared bentonite. Its isolator part i.e oxides can be etched to remove oxides by using a mixture of HF / H₂O / NH₄F or HF / HNO₃ / H₂O or by using CF₄ / H₂ which produces silicon layer that is free from oxide and silicon is then etched with a solution of HF / HNO₃ / CH₃COOH / I₂ so that the silicon will be dissolved. The amount of surface area that is produced depends on the time used for etching. If the time spent too long SiO₂ or Si late at all and thus it is not expected that the time used for etching needs to be controlled [9, 10].

If the etching technique is achieved then the surface and pores become larger pillared bentonite which allegedly produces macrospores pillared bentonite. Pillared by using TiO₂ and etching silicate bentonite can change the physical and chemical properties, increase the basal spacing (D₀₀₀₁), specific surface area, total volume, surface acidity and decrease the average pore spokes.

TiO₂ pillared bentonite can be used as catalysts in the manufacture of hydrogen gas and oxygen from the water, in this study the researchers are interested in examining the provision of this pillared bentonite as catalyst.

Natural bentonite has 60% of its silicon content, to provide this material as a catalyst it is necessary to increase the surface area and pore volume by way of intercalation with TiO₂ and be-TiO₂ pillared bentonite. Titanium metal oxide is a material that is sensitive to light and either be a photochemical catalyst. If TiO₂ pillared bentonite do etching with chemicals then etched pillared bentonite can be co-catalyst. So that needs to be studied preparing a catalyst sensitive to sunlight than natural bentonite and bentonite pillared whether TiO₂ that has been etched can be as a co-catalyst manufacture hydrogen and oxygen gases from water.

Aldehyde group of glucose may experience a reduction in the presence of hydrogen and a catalyst to form a metal hydride into polyalcohols called alditol. Product of the reduction of d-glucose called D-sorbitol or sorbitol [11]. Past research has made the hydrogenation of glucose to sorbitol with different catalysts [12] has made the hydrogenation of glucose 50% at a temperature of 353 K, a pressure of 4 MPa using a Ni catalyst. Clauss, 2006 using a catalyst Ni / SO₂ with glucose 20% at a temperature of 393 K with a pressure of 120 bar. In 2007, Welasih also hydrogenate glucose with Nickel catalyst at a temperature of 95-105° C and a pressure of 60 bars. From the research generated by 0.5963 g sorbitole.

Based on the description above, the researchers are interested to hydrogenate glucose to sorbitol without pressure, high temperature. With the TiO₂ pillared bentonite as producing hydrogen gas from water using UV light from the sun.

2. Experiment

Bentonite clay with a composition of 61.02% SiO₂; 15.21% Al₂O₃; 4.89% Fe₂O₃; 0.62% TiO₂; 2.08% CaO; 1.94% MgO; 0.46% K₂O; 3.45% Na₂O; 10.31% incandescent lost. Based on this, the composition of bentonite District of Padang Tualang, Langkat, types of Na-bentonite. Bentonite is...
sieved to 100 mesh sieve passes are then washed with distilled water several times and filtered by vacuum filtration and dried in an oven at 100°C for 5 hours. After that bentonite clay is dried and crushed into powder and sieved using a 100 mesh sieve.

2.1 Etching TiO$_2$ pillared Bentonite

TiO$_2$ pillared bentonite calcined at a temperature of 400°C is taken as much as 20 g, then put in a plastic container. Etcher solution is then added (a mixture of: 3ml HF (p) + 5ml HNO$_3$ (p) + 3ml CH$_3$COOH (glacial) / I$_2$ of 0.3 g / 250 ml H$_2$O). Then stirred using a plastic stirrer for 10 minutes, then the precipitate is separated from the solution by decantation using a plastic pipette. The precipitate was then dispersed in aqua bidestilate then neutralized pH, decanted using a plastic pipette. Etching products are divided into 3 parts, each furnaced at 400, 450, 500°C for 1 hour. Then the surface area was analyzed.

The results of SEM photos of surface area analyzer indicates that the product is heated at a temperature of 450°C has the most extensive surface area and will be used to test the catalyst/co-catalyst in water.

2.2 Making Hydrogen and Oxygen Gas from Water Using the catalyst/co-catalyst TiO$_2$ pillared Bentonite by UV irradiation Wavelength 180 nm

Bentonite from (3.7) and (3.8) weighed as much as 4 g, then put in a pumpkin that has been filled in 10 ml of distilled water and stirred for 10-15 minutes then measured the pH. Pumpkin is connected with a thermometer and three branch pipes are connected to a manometer. Subsequently irradiated with ultraviolet at a wavelength $\lambda = 180$ nm irradiation carried out for 1-5 days and observed no changes in the manometer. Manometer result of changes in total gas pressure can be calculated total gas (%).

2.3 Sorbitol Hydrogenation

Inserted into a transparent bottle container 2.5 glucose, 0.1 g of nickel powder, 1 g of TiO$_2$ pillared bentonite and 20 ml of distilled water and then sealed. Stirred with a magnetic stirrer and placed under a UV sun rays for 30 days. Then filtered, pH measured and tested with Tollens reagent and Fehling reagents. After that, the filtrate evaporated and sucked up a vacuum to form crystals. Tested melting point and were characterized by FTIR and $^1$H NMR.

3. Results and Discussion

Based on the analysis of the composition of bentonite Kabupaten Langkat then bentonite above include Na-bentonite type or swelling. Bentonite is so dried in an oven at 100 °C and crushed and sieved to 100 mesh sieve. Bentonite is then soaked in 1 M NaCl for 1 week, so going enrichment of Na-bentonite after forming sodium bentonite then put into a 100°C oven until dry and after dry sieved to 100 mesh sieve. The last step enrichment sodium bentonite made by dispersing the Na-bentonite 6 M NaCl solution or saturated NaCl for 24 hours, then washed and dried 100°C, this material is called Na-bentonite.
Table 1 Composition of Bentonite’s Langkat

|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| SiO₂  | 61.02 % | MgO   | 1.94 % |       |
| Al₂O₃ | 15.21 % | K₂O   | 0.46 % |       |
| Fe₂O₃ | 4.89 %  | Na₂O  | 3.45 % |       |
| TiO₂  | 0.62 %  | missing |       | incandescent |
| CaO   | 2.08 %  | Water content |       | 7.07 % |

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Na-bentonite subsequently dispersed into several solution of sulfuric acid 0.5; 1; 1.5; 2 M stirred with a magnetic stirrer, activation carried out for 24 hours, filtered by vacuum filtration and then dried in an oven. Activation is aimed to increase the distance between Na-bentonite layer so that it becomes larger.

Once the distance between the layer of Na-bentonite new enlarged carried intercalation and pillarization where activated Na-bentonite dispersed 0.82 M TiCl₄ complex solution while stirring with a magnetic stirrer for 18 hours. The results of this intercalation separated by a vacuum pump, intekalasion purpose to enter into the complex Ti distances between the bentonite layer, then calcinated at 350 °C to form a more solid oxide pillars.

Analysis was done by X-ray diffraction, using Cu powder radiated by Kα, each 2 grams of TiO₂ pillared bentonite and activated clay filled into a sample and then made diffractogram with \( \lambda = 1.5425 \) Å.

Based on the results of measurement of basal spacing (D001) there was an increase in basal spacing on the TiO₂-pillared bentonite using acid activation of 0.5 and 1.5 M while those using TiO₂ pillared bentonite activation damaged. It can be seen from the X-ray diffraction data. The increase in basal spacing will be followed by an increase in surface area, increased porosity, and total volume.

![Results diffractogram for Na-bentonite Activated with sulfuric acid 1.5 M](image)

**Figure 1.** Results diffractogram for Na-bentonite Activated with sulfuric acid 1.5 M
Table 2 The Na-bentonite is characterized by peaks at 2-theta

| Type of Mineral | d (Å) | 2- Teta |
|-----------------|-------|--------|
| Na–Bentonite    |       |        |
| 14.91           | 5.92  |        |
| 13.88           | 6.36  |        |
| 4.70            | 18.84 |        |
| 3.04            | 29.28 |        |
| Kaolinit        |       |        |
| 8.27            | 10.68 |        |
| 3.57            | 24.88 |        |
| 2.32            | 38.68 |        |
| Quartz          |       |        |
| 4.07            | 21.80 |        |
| 2.51            | 35.68 |        |
| Mica            | 3.34  | 3.34   |

Based on Table 2, the Na-bentonite is characterized by peaks at 2-theta ie: 5.92; 6.36; 18.84; 29.28 with basal spacing d (Å) respectively: 14.91; 13.88; 4.70; 3.04 and other peaks are kaolinite, quartz, mica means bentonite has not been enriched so there are still impurities.

Figure 2. Results diffractograms for TiO$_2$ pillared Bentonite

From this diffractogram (Figure 2) can be given information about changes in the angle theta 6 changes the distance between layers of Na-bentonite into a pillared bentonite-TiO$_2$ for observation or pillared bentonite changes in the angle theta 0-5. From Figure 1 and 2 have been changes in peak intensity and changing the distance between layers D001.

From the X-ray diffraction data above (Figure 1 and 2) can be determined the distance between layers, as well as identification in identifying the types of clay mineral, to calculate the distance between layers (d) mineral bentonite can be used formula Bragg:

\[ n\lambda = 2d \sin \theta \]
\[ d = \frac{n\lambda}{2 \sin \theta} \]
where, \( d \) = the distance between the fields of atomic crystals
\( \lambda \) = wavelength (1 Å = 10-10 m)
\( \theta \) = angle of diffraction
\( n \) = order of diffraction

(a) The distance between layers (d) for the Na-bentonite
\( n = 1 \)
\( \lambda \) = wavelength (1 Å = 10-10 m)
\( 2 \theta = 5.920; \theta = 2.960 \)
\( d = \frac{1 \times 1.5410^{-10}}{2 \sin \theta} \)
\( d = 14.917 \) Å

(b) TiO\(_2\) pillared Bentonite using 1.5 M sulfuric acid can be calculated as follows:
\( n = 1 \)
\( \lambda \) = 1.54 x 10-10 m
\( 2 \theta = 5.920; \theta = 2.960 \)
\( d = 16.9807 \) Å

Further changes in the distance between layers (\( \Delta d \)) are:
\( (\Delta d) = d (b) - d (a) \)
\( = 16.980 \) to 14.916
\( = 2.063 \) Å

Based on X-ray diffraction analysis then by intercalation and pillarization add, increase the porosity of the basal spacing = 2.06 Å.

The pillarization of TiO\(_2\) has increased the distance between the layers of \( d = 2.0633 \) Å. Data analysis is then performed using FT-IR.

![Figure 3. FT-IR absorption spectrum for the Na-Bentonite](image-url)
In the FT-IR spectra have seen a shift wave number around 798 cm\(^{-1}\) to 794 cm\(^{-1}\) is due to the pillared bentonite pillaring process is well established in dispersion 1.5 M sulfuric acid, it is adjusted to the data of X-RD confirming the intercalation and pillarization perfect and this is the best for the pillars. From the data by calculating the surface area analyzer surface area obtained the results as shown in Table 3.

**Table 3. Surface Area and Pore Volume Total of bentonite pillared on condition Acids by Using Equation BET**

| Sulfuric Acid Concentration (M) | Surface Area (m\(^2\)/g) | Total Pores Volume (cc/g) |
|---------------------------------|--------------------------|--------------------------|
| 0.5                             | 83.3018                  | 0.0415                   |
| 1                               | 86.8939                  | 0.0435                   |
| 1.5                             | 89.0563                  | 0.0445                   |
| 2                               | 88.7607                  | 0.0443                   |

Based on the data of three X-RD, FT-IR and visible surface at a concentration of 1.5 M sulfuric acid good for intercalation in pillarization produce physical changes in basal spacing, surface area and total pore volume increases.

Furthermore TiO\(_2\) pillared bentonite activated in best H\(_2\)SO\(_4\) etched using a mixture (28 ml HF + 170 ml H\(_2\)O + 113 g NH\(_4\)F) for 2-10 minutes for etching the oxide on silica and make a lot of holes (H\(^+\)) on silica, then etched using solution (1 ml 5 ml HF + HNO\(_3\) + 2 ml CH\(_3\)COOH + 0.3 g I\(_2\) / 250ml H\(_2\)O) for 5-10 minutes for etching silicon further heated to 400, 450, and 500°C for 1 hour. With such technique will produce pillared bentonite macropore and reproduce (H\(^+\)).

**4. Discussion**

4.1 Preparation of Na-Bentonite

Bentonite samples from the District Padang Tualang, Langkat that have not done enrichment bentonite, made into Na-bentonite produce basal spacing D001 = 14.917 Å, whereas in theory Na-bentonite its basal spacing = 9.8 Å. This means Na-bentonite absorbs water from the humidity so that the measurement time X-ray diffraction to be great. From the X-ray diffraction data (Figure 4.1) clearly show Na-bentonite which still contains kaolinite, quartz and mica. Na-bentonite can be observed a peak at an angle of 0-5 theta, at the height of this is the identity of the Na-bentonite.

4.2 Intercalation and pillarization
Na-bentonite subsequently soaked with sulfuric acid of 0.5-2 M and intercalated using Ti$^{2+}$ then pillared at 350°C. The calcination is useful to form the pillars of oxide on bentonite. Thus forming a TiO$_2$ pillared bentonite. For the identification of pillared bentonite seen from the X-ray diffraction data at an angle 0-5 theta, which turned into a basal spacing 16.9807 Å. This means that the manufacture of the pillared bentonite has been successful in increasing the basal spacing, surface area and pore volume. The study of literature obtained basal spacing of 28.3 Å. This could occur because of the purity of the bentonite is used, meaning that bentonite material is different then produced basal spacing on different pillars.

4.3 Etching TiO$_2$ pillared Bentonite
TiO$_2$ pillared bentonite subsequently etched using a chemical etcher to reproduce hole (h$^+$). Hole in silicate form marked changes in surface area and pore volume of the original. Also, based on the SEM image surface becomes more rugged than ever before.

As a result of ultraviolet radiation $\lambda = 180$ nm, the hydrogen bonding of water will be released and oxygen from water interacting with metal oxides TiO$_2$ and hydrogen from the water molecule will interact with silica. These interactions can lower the activation energy of water molecules. Ultraviolet light enter the pores of bentonite by SiO$_2$ ultraviolet light is converted to shortwave resulting hydrogen and oxygen molecules to break up. Testing of gas generated a total of 78.5% using pillared bentonite etched, while those using TiO$_2$-pillared bentonite gas generated as much as 60.4%.

4.4 Sorbitol FTIR Spectrum
FTIR spectrum of the product (KBr) showed an absorption band at 3391.2 cm$^{-1}$, 2935 cm$^{-1}$, 1646.02 cm$^{-1}$, 1047.39 cm$^{-1}$. Absorption at 3391.2 cm$^{-1}$ region indicates stretching stretching vibration absorption OH OH group that stretched from primary and secondary alcohols. Which supported an absorption band 1418.07 cm$^{-1}$ as buckling OH. Absorption at 2915.7 cm$^{-1}$ region showed the presence of CH and CH$_2$. While the C-O in alcohol produced ribbons region in 1416 and 1047.39 cm$^{-1}$.

5. Conclusion
1. TiO$_2$ pillared Bentonite made from sodium bentonite types can increase the basal spacing, surface area and total pore volume.
2. SiO$_2$ of TiO$_2$ pillared bentonite etched going hole so that the silica is a hollow volume, so it can be as a co-catalyst.
3. TiO$_2$ pillared Bentonite is made in an atmosphere of 1.5 M sulfuric acid can be used as a catalyst manufacture of hydrogen gas.
4. The hydrogen gas produced by TiO$_2$ bentonite in aqueous solvent can be used for the hydrogenation of glucose to sorbitol. Nickel catalysts and irradiation with UV sunlight for 30 days and produced sorbitol as much as 66.8%.

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