Utilizing Imogolite Nanotubes as a Tunable Catalytic Material for the Selective Isomerization of Glucose to Fructose

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Abstract

The isomerization of glucose to fructose is an important step in the conversion of biomass to valuable fuels and chemicals. A key challenge for the isomerization reaction is achieving high selectivity towards fructose using recyclable and inexpensive catalysts. In this study, the isomerization of glucose to fructose is investigated through using using imogolite nanotubes as a catalyst. Imogolite is a single-walled aluminosilicate nanotube characterized by surface areas of 200-400 m^2/g and pore widths near 1 nm. Imogolite is a highly tunable structure and can be modified through substitution of Si with Ge or through functionalization of methyl groups to the inner surface. These modifications change the surface properties of the nanotubes and enable tuning of the catalytic performance. Imogolite nanotubes are successfully used as a heterogeneous catalyst for the isomerization of glucose to fructose. Of the compositions tested, aluminosilicate imogolite is the most active material for the conversion of glucose, achieving a glucose conversion of 30% and a fructose selectivity of 45%. Catalyst recycling experiments reveals that organic content accumulates on the nanotubes that results in a minor reduction in conversion while maintaining similar catalytic selectivity. Overall, imogolite nanotubes are an active and tunable catalytic platform for the isomerization of glucose to fructose.

Keywords: Biomass utilization; glucose isomerization; imogolite; nanotube

1. Introduction

Creating sustainable methods to produce chemicals and fuels can be achieved through identifying robust and stable catalytic materials for conversion of biomass. Indeed, the primary challenge for biomass conversion is achieving high selectivity with a stable heterogeneous catalytic material. One important chemical reaction for biomass conversion is the isomerization of glucose to fructose [1]. This reaction remains an important bottleneck in producing the important intermediate 5-hydroxymethylfurfuraldehyde (HMF), which is considered an important chemical to produce to enable large scale biomass processing [2]. The importance of this overall reaction sequence merits investigation of alternative catalytic materials.

Several intriguing catalysts for this reaction have been investigated, including enzymes [3], Lewis acids [4], inorganic Brønsted bases [5,6], and organic bases [7,8]. The most common industrial catalyst for isomerization of glucose to fructose is the enzyme glucose isomerase.

Though enzymes are widely used for food applications, it is necessary to maintain strict control of pH, temperature, and feed purity to avoid catalyst deactivation [3]. To enable large scale biomass utilization, it is desirable to develop more robust catalytic materials. Seminal work discovered that glucose isomerization could be catalyzed by the Lewis acidic zeolite Sn-Beta [4]. This work has sparked interest in catalysts for the isomerization of glucose to fructose, but commercial utilization would require improving catalyst lifetime since Sn-Beta undergoes deactivation via leaching of Sn active sites [9]. Several inorganic base catalysts have been identified for the reaction including $Ca(OH)_2$ and NaOH [5,6]. The yield of fructose achieved with these catalysts is thought to be low because of the instability of monosaccharides when exposed to high concentrations of base catalysts. Intriguing work has also investigated organic base such as triethylamine [7,8]. Homogeneous triethylamine exhibited good catalytic activity and selectivity, but homogeneous catalysts are more difficult to recycle than heterogeneous catalysts. This work induced researchers to investigate heterogeneous catalysts such as poly(ethylene imine) (PEI) [7] and tertiary amines immobilized on silica materials [8]. These catalysts tended to deactivate via leaching and formation of an acidic byproduct that is currently unknown, though the catalysts could be regenerated through washing with pure water. Combining the ideas of using zeolites and base catalyst, researchers have investigated sodium-exchanged zeolites [10]. These catalysts are active and selective, but deactivate via leaching of the basic sodium species, making constant regeneration of the active site necessary. The concept of base catalyzed glucose isomerization certainly has merit, provided that the deactivation could be limited.

An interesting alternative material that has received limited investigation is imogolite. Imogolite is a naturally occurring aluminosilicate nanotube with an empirical formula of $(OH)_3Al_2O_3SiOH$ that was first discovered in 1962 in volcanic-ash derived soils in Japan [11]. A synthetic procedure was first described in 1977 based upon the conditions in which imogolite formed [12]. This procedure has been optimized over the years, and it can be synthesized with monodisperse and tunable dimensions and composition [13–15]. Imogolite nanotubes have a diameter of 2 nm and range in length from 100 to 1000 nm. Currently, limited characterization has been performed to determine the nature of the surface properties of the catalytic materials.

Several modifications have been performed on imogolite that could provide the ability to control its properties on the nanoscale. Aluminogermanate imogolite has been synthesized with up to 100% substitution of silicon with germanium. The resulting nanotubes have larger, tunable diameters and can form double-walled nanotubes [14,16,17]. Interior surface modification with organic groups has also been performed using acetyl chloride, methyltrimethoxysilane, and trichloro-silane [15]. The organic groups adjust the composition, hydrophobicity, and dimensions of the nanotube. Iron-doped imogolite has been synthesized as a potential catalyst for oxidation reactions [18]. Gold nanoparticle and imogolite composites have been fabricated for use as a catalyst or a coloring agent [19]. Additionally, silver nanoparticles were immobilized on imogolite and showed antibacterial properties [20]. It has also been shown that the phosphate groups of DNA interact with the aluminol groups on imogolite, which was utilized to form imogolite/DNA hybrid hydrogels [21]. These different compositions suggest that imogolite is a tunable platform.

The high level of modification offered by imogolite can serve as a tunable catalytic platform. Yet, little work has been done on application of imogolite nanotubes, especially in the realm of catalysis [22,23]. To evaluate the promise that imogolite holds as tunable heterogeneous catalytic platform, it is important to elucidate structure-function relationships of the modifications that have been performed. Identification of design elements of imogolite would offer the ability to tune its properties and enable its use as an effective catalytic platform.

In this work, imogolite is investigated as a catalyst for the selective isomerization of glucose to fructose. The work examines the effect of modifying the composition of the imogolite nanotubes through including germanium and methyl substitution to alter the surface properties and catalytic performance. The most selective material is subjected to recycle experiments to determine the robustness of the catalytic material. Overall, this work provides insight on the catalytic activity in imogolite and its potential as a tunable, heterogeneous catalytic platform.

2. Experimental Methods

2.1. Chemicals

The following chemicals are used and stored in a glovebox: tetraethylorthosilicate (TOES; 98%, Acros Organics), germanium(IV) ethoxide (97%, BeanTown Chemical), aluminum-tri-sec-butoxide (95%, Alfa Aesar), methyltrimethoxysilane (97%, Alfa Aesar). The following chemicals are also used: perchloric acid (70% by wt., BDH), hydrochloric acid (36.5-38%, BDH), ammonia

(28-30%, Sigma Aldrich), dextrose (USP grade, Fisher), and D-mannitol (99%, Amresco). De-ionized (DI) water is obtained by a house supply that produces Milli-Q quality water.

2.2. Imogolite Synthesis

The synthesis of imogolite nanotubes has been achieved through methods described previously [24]. Perchloric acid is diluted to 38 mM from a 70 wt% (11.6 M) stock solution. A solution is made with 5.454 g of 70 wt% perchloric acid ($HClO_4$) and 1000 mL of DI water. Precursors to imogolite are mixed in a glove box filled with nitrogen. For aluminosilicate imogolite (Al-Si IMO), aluminum-tri-sec-butoxide (4.680 g) is mixed with TEOS (1.979 g) in a glass vial and shaken vigorously. This precursor mixture is then added to a 38 mM $HClO_4$ solution (250 mL) in a 2 L round-bottom flask under stirring at room temperature. The final molar ratio is Si:Al:$HClO_4$ of 1:2:1. The solutions are stirred at room temperature for 24 h. The solution is then diluted by a factor of 3.8 with DI water (700 mL) and stirred at 95°C for 4 days. After this period, the solution is allowed to cool to room temperature and concentrated using one of two methods. The first method involves concentrating the reaction mixture by a factor of 10 to approximately 100 mL using a rotary evaporator. Materials concentrated using a rotary evaporator are labeled with "R". All materials modified with germanium and methyl functionalization are concentrated using the rotovap method. For the second method of concentration, a 30 wt% ammonia solution is added dropwise until gelation of the nanotube solution occurs and a pH of 10 is reached. The gels are then centrifuged at 9000 rpm for 10 min and the supernatant is discarded. The nanotubes are dispersed by adding a few drops of hydrochloric acid to the gel, which results in some fuming to be observed. Materials concentrated using this acid-base addition method are labeled with "AB". The gels obtained by both methods are added to a 15,000 kDa membrane submerged in DI water. The water is exchanged daily for 5 days. The purified gels are dried at 80°C, and the resulting solids are ground vigorously to obtain imogolite nanotubes as a fine powder.

For germanium imogolite (Ge-x-IMO), aluminum-tri-sec-butoxide is mixed with germanium(IV) ethoxide and tetraethylorthosilicate in a molar ratio of Si:Ge:Al:$HClO_4$ of (1-x):x:2:1. For Ge-0.3-IMO, this corresponds to combining 4.680 g aluminum-tri-sec-butoxide, 0.721 g germanium(IV) ethoxide, and 1.385 g TEOS. For Ge-0.8-IMO, the mixture consists of 4.680 g aluminum-tri-sec-butoxide, 1.922 g germanium(IV) ethoxide, and 0.396 g TEOS. For methyl imogolite (Me-x-IMO), aluminum-tri-sec-butoxide is mixed with methyltrimethoxysilane

(Me-Si) and tetraethylorthosilicate in a molar ratio of Si:Me-Si:Al:$HClO_4$ of (1-x):x:2:1. For Me-0.5-IMO, this corresponds to 4.680 g aluminum-tri-sec-butoxide, 0.647 g methyltrimethoxysilane, and 0.990 g TEOS. For Me-1.0-IMO, the mixture consists of 4.680 g aluminum-tri-sec-butoxide and 1.294 g methyltrimethoxysilane.

2.3. Material Characterization

The materials are characterized using standard techniques, including nitrogen physisorption, X-ray diffraction (XRD), and thermogravimetric analysis with differential scanning calorimetry (TGA-DSC). The textural properties are analyzed using a Micromeritics 3Flex surface characterization analyzer. Before analysis, the materials are degassed at 250°C using the SmartVac Prep. The surface area is calculated using the BET method and the pore size is calculated using the HK method. Powder X-ray diffraction data are collected on a Bruker D8 Advance powder diffractometer (40 kV, 40 mA, sealed Cu X-ray tube) equipped with a Lynxeye XE-T position sensitive detector in Bragg-Brentano geometry. TGA-DSC are performed using STA 449 F5 Jupiter® (NETZSCH Instruments). The analysis is performed under flowing air (20 mL/min) and nitrogen (20 mL/min) at a ramp rate of 10°C/min from 30°C to 900°C followed by a 5 min hold at 900°C.

Methanol pulse experiments are conducted using a homebuilt system coupled with an MKS Cirrus bench-top residual gas analyzer. The samples (10 mg of each catalyst) are packed in a ¼ in OD quartz tube reactor placed in a tubular furnace. Helium is used as carrier gas at a flow rate of 30 sccm, passing the stream through a methanol bubbler that is maintained at room temperature to produce a vapor concentration of 16% CH_3OH in He. This stream is passed into a 500 µL sample loop attached to a 6-port valve that can be switched with a manual actuator. After filling the sample loop with methanol saturated helium, the valve is actuated to send the methanol containing pulse to the sample. The exit stream is analyzed using an MKS Cirrus bench-top residual gas analyzer. Pulses are sent until three equal-area peaks are observed in MS signal m/z=31, which indicates that the surface is saturated with methanol.

2.4. Catalytic Testing

As illustrated in Scheme 1, catalytic testing is performed using a method that is similar to previous work [8]. A bulk solution containing 4.0 g glucose and 36.0 g DI water is prepared. One gram of the bulk solution is combined with 100 mg of catalyst in a 5 mL pressure tube. The tubes are submerged in a silicone oil bath at 100°C at 420 rpm. After 24 hours, the tubes are transferred to an ice bath for 15 min. The solution is diluted with 2 g of 0.3 M d-mannitol solution (internal standard for HPLC measurements) and 30 g of DI water. The solution is centrifuged at 9000 rpm for 15 min and the supernatant is filtered using a 0.22 µm nylon (Ø = 13 mm) syringe filter. The filtered solution is analyzed using High Performance Liquid Chromatography (HPLC) from Waters (Acquity) equipped with a Waters Sugar Pak-1 column (including pre-column filter) and refractive index (RI) detector. DI water is used as the mobile phase at a flow rate of 0.20 mL/min and a column temperature of 70°C. This analysis is used to quantify the concentrations of glucose, fructose, and mannitol. The selectivity of the catalyst is calculated as the amount of fructose produced per amount of glucose converted.

2.5. Catalyst Reuse Testing

Catalyst reuse testing is also performed to evaluate the ability to recycle the catalytic materia. The reaction began with 300 mg of catalyst and 3.0 g of 10 wt% glucose solution. Following the reaction, the solution is diluted and centrifuged at 9000 rpm for 15 minutes, as described previously. The supernatant is completely removed to separate the catalyst. DI water (25 mL) is added, and the centrifugation step is repeated. This step is performed two additional times for a total of three washes. The catalyst is dried overnight at 80°C. The mass of the catalyst is obtained through weighing the recovered material and then added to an amount of 10 wt% glucose solution that corresponds to 100 mg catalyst per gram of 10 wt% glucose solution.

Acid and base treatment are applied in separate tests to regenerate the catalyst after a single reaction. Post reaction, the catalyst is recovered through centrifugation, as described above. For acid treatment, 100 mL of a 1.0 M HCl solution is prepared. For base treatment, 100 mL of a 1.0 M NH_4OH solution is prepared. A solution of either acid or base (25 mL) is added to 50 mg of dried catalyst obtained after a single reaction. The solution is mixed and then centrifuged at 9000 rpm for 15 minutes. The supernatant is completely removed to separate the catalyst. An additional 25 mL of acid or base solution is added for a total of four washes. DI water (25 mL) is added and the centrifugation step is repeated. This step is performed two additional times for a total of three DI water washes. The catalyst is dried overnight at 80°C prior to TGA/DSC measurements.

3. Results and Discussion

3.1. Catalyst Synthesis and Characterization

Imogolite nanotubes are successfully synthesized utilizing the procedure described previously [24]. For all variations of imogolite, the solution turns cloudy upon combination of precursors and the $HClO_4$ solution. For the Al-Si and Ge-IMO, the solution then turns clear approximately one hour after heating to 95°C. The Me-IMO remains cloudy throughout the synthesis, potentially because of the increased hydrophobicity of the material [15]. Concentration via the rotovap method yields a cloudy solution whereas the acid-base method yields a gel-like solution. After drying, both result in a sheet-like material that must be ground vigorously to yield imogolite as a fine powder.

The different imogolite nanotubes are characterized using standard techniques such as powder XRD and nitrogen physisorption. The XRD pattern of Al-Si IMO is compared to Ge- and Me-IMO in Figure 1. The important characteristic peaks of imogolite occur near 4, 9, 13, 28, and 40° 2θ. The characteristic peaks of imogolite remain in the Ge-IMO samples. New peaks begin to form near 10° for 30% Ge and increase in intensity at 80% Ge, which are consistent with previous attempts to synthesize Ge-IMO [14,25]. The shift of the first peak to smaller 2θ indicates an increase in the inner diameter of the nanotube that is expected since Ge is a larger heteroatom, requiring a larger radius of curvature. The Me-IMO patterns in Figure 1 contain the characteristic peaks of imogolite. With increasing methyl content, a sharp feature forms near 20° that indicates long-range order or crystallinity. The presence of the characteristic peaks are consistent with the formation of imogolite nanotubes. For the Me-IMO samples, it can be seen in the peaks at 4 and 9° that sharpness and intensity increase, demonstrating further evidence of increased pore ordering.

The effects of composition on surface area and pore properties of imogolite are analyzed with nitrogen physisorption (Figure S1). Table 1 provides a summary of imogolite materials analyzed with nitrogen physisorption along with sites per surface area analyzed with methanol pulse experiments. A single synthesis mixture of AlSi imogolite is split into two to analyze the effect of the concentration method on the surface properties of imogolite. For the rotovap method, the sample has a surface area of 273 m^2/g with a pore width of 0.88 nm. For the acid-base method, the surface area is 288 m^2/g with a pore width of 0.88 nm. These results demonstrate that the method of concentration does not have a significant impact on the surface properties of imogolite.

Germanium substitution results in changes to the surface area and pore width (Figure S1; Table 1). The surface area of Ge-IMO is lower than that of AlSi IMO. Introduction of Ge into IMO also results in an increased pore width according to nitrogen physisorption, which is corroborated by the shift to the left in the first peak of the XRD patterns. At 30% Ge, a pore width of 0.91 nm is achieved, which is greater than the pure IMO. The pore width further increases to 0.95 nm for 80% Ge. The increase in pore width can be explained by the increase in bond length from Si-O to Ge-O, as has been previously reported [26], and is consistent with XRD results.

Methyl substitution leads to an increase in pore size from 0.94 nm at 50% methyl to 1.10 nm at 100% methyl (Figure S2; Table 1). The increased pore size could be attributed to the presence of methyl groups on the inner surface of the nanotubes. The surface areas for these materials are generally higher than Al-Si IMO, 456 and 366 m^2/g at 50% and 100% methyl, respectively. This increase may result from the increased hydrophobicity of the material. TGA-DSC measurements indicate that a lower mass loss for temperature less than 200°C for the methyl substituted materials (Figure S3 and S4). Though all materials undergo heating under vacuum to remove any adsorbed compounds, it is possible water remains more strongly adsorbed to pure imogolite than the modified materials [15]. Indeed, it has been shown previously that the degas temperature has a strong effect on measured surface area. While heating can help remove water, it can also cause irreversible structure collapse [27]. Therefore, a consistent temperature of 250°C is used for all sample degassing.

3.2. Glucose to Fructose Isomerization Results

Catalytic performance is evaluated through testing kinetic performance of AlSi imogolite concentrated using the rotovap method. Figure 2 depicts the observed conversion and selectivity at different time points over 48 hours for IMO-R. Conversion steadily increases with time and selectivity decreases with time. Although the isomerization of glucose to fructose is an equilibrium-limited reaction, an equilibrium composition of glucose and fructose is not achieved using an imogolite catalyst. This test also demonstrates the activity of imogolite for the isomerization of glucose. After 48 hours, the imogolite catalyst converts 35% of the glucose with 40% selectivity for fructose. Conversion continues to increase at 48 hours, providing evidence the sites are not poisoned and the catalyst does not undergo deactivation, unlike previous organic amine based catalysts [8].

The accessible surface area on the outer wall of the nanotube, comprised of a gibbsite sheet, provides the most likely source of the catalytic activity for imogolite. The outer wall of imogolite is comparable to a gibbsite [$Al(OH)_3$] sheet [27,28]. Gibbsite, which is a mineral form of aluminum hydroxide, displays amphoteric behavior [29]. In acidic conditions, gibbsite behaves as a Brønsted base whereas in basic conditions, imogolite behaves as a Lewis acid. As mentioned previously, both Brønsted basic and Lewis acidic catalysts are active for the isomerization of glucose to fructose. Therefore, the pH of the reaction mixture is measured at different points during the reaction. Before adding the catalyst, the pH of the glucose solution is slightly below neutral corresponding to 6.3. After adding the catalyst, the pH decreases further, resulting in a pH of 3.4. After the reaction, the solution pH is 3.0, indicating that acidic species are formed during the reaction. Overall, the pH measurements suggest that the catalyst is acting as a Brønsted base during the reaction.

The effect of concentration method for AlSi imogolite on catalytic activity is studied. At 100°C, no difference is observed in the conversion and selectivity of imogolite concentrated using the rotovap and acid-base methods, as shown in Figure 3. The reaction is also run under inert nitrogen atmosphere. Previous work has found that the selectivity results are sensitive to the presence of air [8]. Relative to air, running the reaction under inert conditions decreases the observed conversion from 30% to 18% and selectivity increases from 45% to 57% in 24 h. Although the selectivity is higher, this selectivity is at a lower conversion. Comparing the results under nitrogen and under air, it is found that all of the results lie along a general trend that is decreasing selectivity at higher conversions.

The imogolite catalyst is also tested at the temperature of 120°C to increase the glucose conversion achieved in 24 hours. This temperature is also convenient since it is the temperature commonly used for fructose dehydration to HMF, a reaction that is commonly coupled with glucose isomerization [30]. At the temperature of 120°C, the imogolite catalyst achieved a conversion of 74%, which is higher than the conversion achieved in 48 hours at 100°C. In addition, imogolite is able to produce a selectivity of 22% to fructose. In comparison to catalytic results at 100°C, the selectivity appears lower at 120°C, but the reaction mixture is also found to contain the fructose dehydration product of HMF with an approximate 5-8% yield of HMF. This yield of HMF indicates more fructose is being produced, but that the fructose is being dehydration to HMF. It is likely that fructose dehydration is not catalyzed by imogolite, but rather occurs in the absence of a catalyst, as concurrent work in our lab will demonstrate (unpublished).

The two modifications to imogolite investigated for effect on catalytic activity are replacing silicon with germanium and replacing the internal silanols with methyl groups. Adding germanium to the framework affects both the curvature of the material and the electronic properties of the material. Catalytic testing of the material with the 30% germanium material (Ge-0.3-IMO) reveals a decrease in the conversion. The selectivity for fructose is lower than other materials at similar conversion. For Ge-0.8-IMO, the conversion is further decreased and the selectivity is increased to 58%, compared to 45% for AlSi IMO. The decrease in activity may be explained by the formation of double-walled nanotubes with Ge-0.8-IMO. The decreased conversion and increased selectivity for Ge-0.8-IMO fits well with the general trend established in Figure 3.

Functionalization of imogolite with methyl groups also has an effect on the catalytic activity. At low temperatures, the conversion of glucose is greatly decreased to 12% for Me-0.5-IMO with a high selectivity of 64%. This data again falls along the linear trend discussed previously, where selectivity increases as conversion decreases. While all other catalytic materials fall along the same trend line, Me-1.0-IMO deviates from the trend established in Figure 4. Me-1.0-IMO has similar conversion to AlSi imogolite, but at much lower selectivity for fructose. The origin of the difference in conversion is investigated through using methanol titration experiments. The methanol titration experiments allow quantification of the total active sites [31]. The titration experiments reveal that the methyl substituted imogolite nanotubes have fewer catalytic sites than the pure IMO materials, as shown in Table 1. Fewer sites would result in lower catalytic activity for Me-0.5-IMO. For the highest methyl-substituted material (Me-1.0-IMO), the methanol titration experiments indicate the lowest number of catalytic sites, but this material is found to have similar conversion as pure AlSi IMO. These results suggest that the methyl substitution is altering catalytic sites in the material to produce less selective sites. The observed change could be associated with the change in curvature of the material.

In general, the modification of imogolite has an effect on the structure and catalytic activity of the material that leads to decreased conversion of glucose with higher selectivities for fructose. It is hypothesized the aluminol groups on the outer wall of the nanotube play a key role in the catalytic activity of imogolite. With 100% methyl substitution, the material still demonstrates catalytic activity. This provides evidence that silanol groups are not necessary for imogolite to convert glucose into fructose. Further investigation of imogolite and its active sites may lend to its use as an effective heterogeneous catalyst for other important reactions. Here, it is demonstrated that imogolite nanotubes are an effective catalyst for the isomerization of glucose to fructose. Formation of HMF is a promising indication of its use as a catalyst for the dehydration of fructose to HMF. Typically, the heterogeneous nature of the catalyst would also be tested through performing a hot filtration test. However, attempts to separate the imogolite catalyst via filtration proved to be difficult. Even during catalyst synthesis, it is found that filtration is difficult. Therefore, the heterogeneous nature of the catalyst will be demonstrated through catalyst reuse testing.

3.3. Catalyst Reuse Testing

Catalyst reuse experiments are used to test the robustness of aluminosilicate imogolite as a catalyst. Since this testing requires collecting the material after a fixed amount of reaction time, it is useful to scale up the initial amount of catalyst to ensure recovery of sufficient material for subsequent tests. The recycle tests are performed at 100°C for 24 hours, achieving a conversion of 25% with a selectivity of 56%, similar to reactions performed at smaller scale. After the reaction, the catalyst is separated from the reaction mixture through centrifugation. The material is washed with distilled water and centrifuged three times before drying in the oven.

After drying in the oven, the catalyst is tested in a second reaction. The recovered material is combined with the fructose solution, maintaining a ratio of catalyst to reaction mixture of 100 mg to 1 g of 10 wt% fructose. For the second 24 hour reaction cycle, the catalyst achieves a conversion of 21% with a selectivity of 49%. Compared to the first reaction cycle, the conversion and the selectivity remain similar to the performance of the fresh catalyst. A third reaction cycle results in conversion of 17% with a selectivity of 49%. These results indicate that the catalytic activity is decreasing, but the catalyst remains selective for the isomerization of glucose to fructose.

Following the three reactions, the catalyst is characterized to provide insight on the observed decrease in conversion. Nitrogen physisorption (Figure S5) reveals a significant decrease in surface area to 95 m^2/g from 288 m^2/g. Interestingly, the isotherm reveals loss of micropore volume associated with the internal pores of the imogolite nanotubes where the silanols are present.

The measured pore width also decreased to 0.71 nm from 0.88 nm. It is also observed that the material changed color from white to brown after the reactions. It is hypothesized organic species adsorb to the inner surface and are not removed during the washing and centrifugation steps. The adsorbed species would both decrease the surface area and reduce the amount of actual catalytic material that would be added during the recycle experiments, reducing the observed conversion. Since the decrease in surface area is much larger than the decrease in conversion, the results are consistent with adsorption of organic species inside the nanotubes on sites that have limited or no catalytic activity. This further corroborates the previous results that the catalytic activity is associated with the external surface of imogolite.

TGA/DSC is performed to compare the quantity and composition of adsorbed species on the imogolite catalyst. Figures 4 display the TGA data for the as-synthesized IMO and the recycled IMO after three reactions. The mass loss of the recycled IMO is much greater than the as-synthesized material, indicative of more adsorbed species on the material. DSC reveals less water is adsorbed on the recycled imogolite and indicates additional organic species adsorbed onto the recycled material. The results of TGA/DSC corroborate the hypothesis generated from the physical appearance of the material and decrease in surface area. The results of the reuse testing could be promising for flow reactors if the organic species catalyst could be removed from the surface of the catalyst.

TGA results can typically be used to identify the calcination temperature required to regenerate the catalyst. However, the imogolite nanotubes are known to collapse irreversibly at temperatures greater than 300°C [32]. As an alternative, it is examined how different treatments can be used to desorb organic species. It is found that acid treatment using 1 M HCl, caused the material to suspend in solution, making it difficult to separate using filtration or centrifugation. The solubility of imogolite in acidic solution is consistent with the synthesis conditions since imogolite must be concentrated or gelled out of a clear acidic solution. Thus, acid treatment is determined to not be a viable route for imogolite regeneration. Importantly, treatment with a 1 M solution of ammonium hydroxide allowed the material to be separated using centrifugation. TGA of the base-treated material compared to the untreated material is shown in Figure 4. The base-treated imogolite has more adsorbed water, but lower amounts of adsorbed organic species. This is a promising result that shows a potential route to catalyst regeneration through treatment with dilute NH_4OH.

4. Summary

The catalytic activity of imogolite nanotubes is investigated for the selective conversion of glucose to fructose. The selectivity for fructose decreases as the conversion of glucose increases. Introduction of methyl groups or germanium changes the surface properties and catalytic activity of the material, resulting in a lower catalytic activity and/or selectivity than the aluminosilicate IMO. Testing of imogolite nanotubes in reuse experiments show organic species accumulate in imogolite. The catalyst still maintains selectivity for glucose isomerization to fructose even after catalyst reuse. Post-reaction characterization reveals a decrease in surface area and an increase in adsorbed organic species. Treatment with dilute base appears to desorb these species and could be used to regenerate imogolite for further reaction. Overall, these results demonstrate that imogolite could be used as a recyclable heterogeneous catalyst for glucose isomerization.

Keywords

Biomass; Glucose isomerization; Imogolite; aluminosilicate material; Surface characterization

Abbreviations

- IMO = imogolite
- AlSi = aluminosilicate

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Conflict of Interest Statement

The authors have no conflicts of interest to declare.

Supplementary Data

Supplementary data includes nitrogen physisorption and TGA data for the materials used in this manuscript.

References

[1] L. Shuai, J.S. Luterbacher, Organic Solvent Effects in Biomass Conversion Reactions, ChemSusChem. 9 (2015) 133–155. doi:10.1002/cssc.201501148.

[2] Y. Roman-Leshkov, J.N. Chheda, J.A. Dumesic, Phase modifiers promote efficient production of hydroxymethylfurfural from fructose, Science. 312 (2006) 1933–1937. doi:10.1126/science.1126337.

[3] S.H. Bhosale, M.B. Rao, V. V Deshpande, Molecular and industrial aspects of glucose isomerase., Microbiol. Rev. 60 (1996) 280–300.

[4] M. Moliner, Y. Roman-Leshkov, M.E. Davis, Tin-containing zeolites are highly active catalysts for the isomerization of glucose in water, Proc. Natl. Acad. Sci. 107 (2010) 6164–6168. doi:10.1073/pnas.1002358107.

[5] B.Y. Yang, R. Montgomery, Alkaline degradation of glucose: effect of initial concentration of reactants, Carbohydr. Res. 280 (1996) 27–45. doi:10.1016/0008-6215(95)00294-4.

[6] M. Watanabe, Y. Aizawa, T. Iida, T.M. Aida, C. Levy, K. Sue, H. Inomata, Glucose reactions with acid and base catalysts in hot compressed water at 473 K, Carbohydr. Res. 340 (2005) 1925–1930. doi:10.1016/j.carres.2005.06.017.

[7] C. Liu, J.M. Carraher, J.L. Swedberg, C.R. Herndon, C.N. Fleitman, J.-P. Tessonnier, Selective Base-Catalyzed Isomerization of Glucose to Fructose, ACS Catal. 4 (2014) 4295–4298. doi:10.1021/cs501197w.

[8] N. Deshpande, L. Pattanaik, M.R. Whitaker, C.-T. Yang, L. Lin, N.A. Brunelli, Selectively converting glucose to fructose using immobilized tertiary amines, J. Catal. 353 (2017) 205–210. doi:10.1016/j.jcat.2017.07.021.

[9] N. Rajabbeigi, A.I. Torres, C.M. Lew, B. Elyassi, L. Ren, Z. Wang, H. Je Cho, W. Fan, P. Daoutidis, M. Tsapatsis, On the kinetics of the isomerization of glucose to fructose using

Sn-Beta, Chem. Eng. Sci. 116 (2014) 235–242. doi:10.1016/j.ces.2014.04.031.

[10] C. Moreau, R. Durand, A. Roux, D. Tichit, Isomerization of glucose into fructose in the presence of cation-exchanged zeolites and hydrotalcites, Appl. Catal., A. 193 (2000) 257. doi:10.1016/S0926-860X(99)00435-4.

[11] N. Yoshinaga, S. Aomine, Allophane in some ando soils, Soil Sci. Plant Nutr. 8 (1962) 6–13. doi:10.1080/00380768.1962.10430983.

[12] V.C. Farmer, A.R. Fraser, J.M. Tait, Synthesis of imogolite: a tubular aluminium silicate polymer, J. Chem. Soc. Chem. Commun. (1977) 462. doi:10.1039/c39770000462.

[13] S.M. Barrett, P.M. Budd, C. Price, The synthesis and characterization of imogolite, Eur. Polym. J. 27 (1991) 609–612. doi:10.1016/0014-3057(91)90144-D.

[14] S. Mukherjee, V. Bartlow, S. Nair, Phenomenology of the growth of single-walled aluminosilicate and aluminogermanate nanotubes of precise dimensions, Chem. Mater. 17 (2005) 4900–4909. doi:10.1021/cm0505852.

[15] D.-Y. Kang, J. Zang, C.W. Jones, S. Nair, Single-Walled Aluminosilicate Nanotubes with Organic-Modified Interiors, J. Phys. Chem. C. 115 (2011) 7676–7685. doi:10.1021/jp2010919.

[16] S. Wada, K.O.J. Wada, Effects of Substiution of Germanium for Silicon in Imogolite, Clays Clay Miner. 30 (1982) 123–128.

[17] A. Thill, P. Maillet, B. Guiose, O. Spalla, L. Belloni, P. Chaurand, M. Auffan, L. Olivi, J.C. Rose, Physico-chemical control over the single- or double-wall structure of aluminogermanate imogolite-like nanotubes., J. Am. Chem. Soc. 134 (2012) 3780–6. doi:10.1021/ja209756j.

[18] M. Ookawa, M.W.A.J. Anabe, M. Suzuki, Synthesis and Characterization of Fe Containing Imogolite, Energy. 284 (2006) 280–284. doi:10.11362/jcssjclayscience1960.12.Supplement2_280.

[19] Y. Kuroda, K. Fukumoto, K. Kuroda, Uniform and high dispersion of gold nanoparticles on imogolite nanotubes and assembly into morphologically controlled materials, Appl.

Clay Sci. 55 (2012) 10–17. doi:10.1016/j.clay.2011.07.004.

[20] G. Ipek Yucelen, R.E. Connell, J.R. Terbush, D.J. Westenberg, F. Dogan, Synthesis and immobilization of silver nanoparticles on aluminosilicate nanotubes and their antibacterial properties, Appl. Nanosci. 6 (2015) 607–614. doi:10.1007/s13204-015-0467-x.

[21] N. Jiravanichanun, K. Yamamoto, K. Kato, J. Kim, S. Horiuchi, W.O. Yah, H. Otsuka, A. Takahara, Preparation and characterization of imogolite/DNA Hybrid Hydrogels, Biomacromolecules. 13 (2012) 276–281. doi:10.1021/bm201616m.

[22] S. Imamura, T. Kokubu, T. Yamashita, Y. Okamoto, K. Kajiwara, H. Kanai, Shape-selective copper-loaded Imogolite catalyst, J. Catal. 160 (1996) 137–139. doi:10.1006/jcat.1996.0132.

[23] S. Imamura, Y. Hayashi, K. Kajiwara, H. Hoshino, C. Kaito, Imogolite: a possible new type of shape-selective catalyst, Ind. Eng. Chem. Res. 32 (1993) 600–603. doi:10.1021/ie00016a005.

[24] D.-Y. Kang, N.A. Brunelli, G.I. Yucelen, A. Venkatasubramanian, J. Zang, J. Leisen, P.J. Hesketh, C.W. Jones, S. Nair, Direct synthesis of single-walled aminoaluminosilicate nanotubes with enhanced molecular adsorption selectivity, Nat. Commun. 5 (2014) 1–9. doi:10.1038/ncomms4342.

[25] C. Levard, A. Masion, J. Rose, E. Doelsch, D. Borschneck, L. Olivi, P. Chaurand, C. Dominici, F. Ziarelli, A. Thill, P. Maillet, J.Y. Bottero, Synthesis of Ge-imogolite: influence of the hydrolysis ratio on the structure of the nanotubes, Phys. Chem. Chem. Phys. 13 (2011) 14516–14522. doi:10.1039/c1cp20346k.

[26] S. Konduri, S. Mukherjee, S. Nair, Controlling nanotube dimensions: Correlation between composition, diameter, and internal energy of single-walled mixed oxide nanotubes, ACS Nano. 1 (2007) 393–402. doi:10.1021/nn700104e.

[27] W.C. Ackerman, D.M. Smith, J.C. Huling, Y.W. Kim, J.K. Bailey, C.J. Brinker, Gas Vapor Adsorption in Imogolite - a Microporous Tubular Aluminosilicate, Langmuir. 9 (1993) 1051–1057.

[28] P.D.G. Cradwick, V.C. Farmer, J.D. Russell, C.R. Masson, K. Wada, N. Yoshinaga,

Imogolite, a Hydrated Aluminium Silicate of Tubular Structure, Nat. Phys. Sci. 240 (1972) 187–189. doi:10.1038/physci240187a0.

[29] X. Yang, Z. Sun, D. Wang, W. Forsling, Surface acid-base properties and hydration/dehydration mechanisms of aluminum (hydr)oxides, J. Colloid Interface Sci. 308 (2007) 395–404. doi:10.1016/j.jcis.2006.12.023.

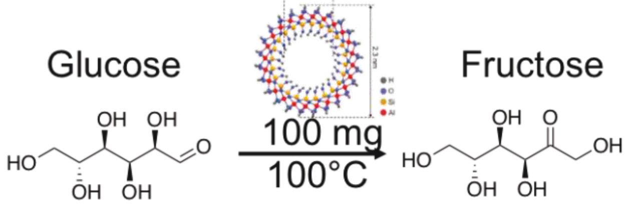
[30] S.G. Wettstein, D. Martin Alonso, E.I. Gurbuz, J.A. Dumesic, A roadmap for conversion of lignocellulosic biomass to chemicals and fuels, Curr. Opin. Chem. Eng. 1 (2012) 218–224. doi:10.1016/j.coche.2012.04.002.

[31] M. Badlani, I.E. Wachs, Methanol: A “smart” chemical probe molecule, Catal. Letters. 75 (2001) 137–149. doi:10.1023/A:1016715520904.

[32] D. Kang, J. Zang, E.R. Wright, A.L. Mccanna, C.W. Jones, S. Nair, Dehydration, Dehydroxylation, and Rehydroxylation of Single-Walled Aluminosilicate Nanotubes, ACS Nano. 4 (2010) 4897–4907.

[33] J.M. de Bruijin, A.P.G. Kieboom, H. van Bekkum, Alkaline degradation of monosaccharides V: Kinetics of the alkaline isomerization and degradation of monosaccharides, Recl. Trav. Chim. Pays-Bas. 106 (1987) 35–43.

[34] J.M. de Bruijin, A.P.G. Kieboom, H. van Bekkum, Alkaline Degradation of Monosaccharides. Part VII. A Mechanistic Picture, Starch-Stärke. 39 (1987) 23–28.



Scheme 1. Isomerization of glucose to fructose.Cross-section of an aluminosilicate imogolite nanotube with average inner and outer diameters labeled [15].

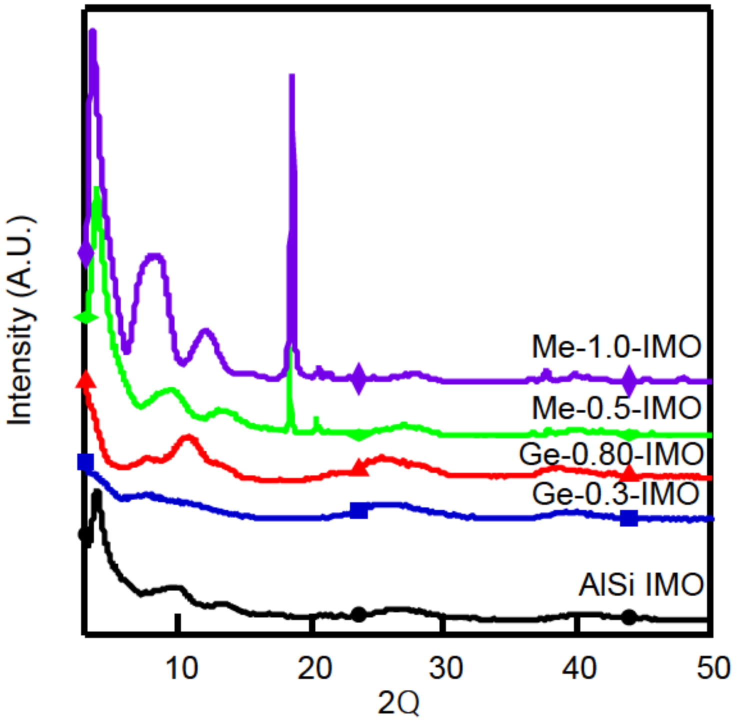


Figure 1. Powder X-ray diffraction pattern of AlSi imogolite (black) compared to Ge-IMO of 30% (blue) and 80% (red) and Me-IMO of 50% (green) and 100% (purple).

Table 1. Nitrogen physisorption and methanol pulse experiment results for imogolite. The surface area BET surface areas and HK pore widths of the AlSi IMO are compared to the Me and Ge modified materials. Sites per surface area and per gram determined by methanol pulse experiements.

Material	BET Surface Area (m^2/g)	HK Pore Width (nm)	Sites per Surface Area (μmol/m^2)	Sites per Gram (mmol/g)
IMO-R	273	0.88	2.5	0.66
IMO-AB	288	0.88	-	-
Me-0.5-IMO	456	0.94	0.98	0.40
Me-1.0-IMO	366	1.10	0.28	0.10
Ge-0.3-IMO	229	0.91	-	-
Ge-0.8-IMO	253	0.95	-	-

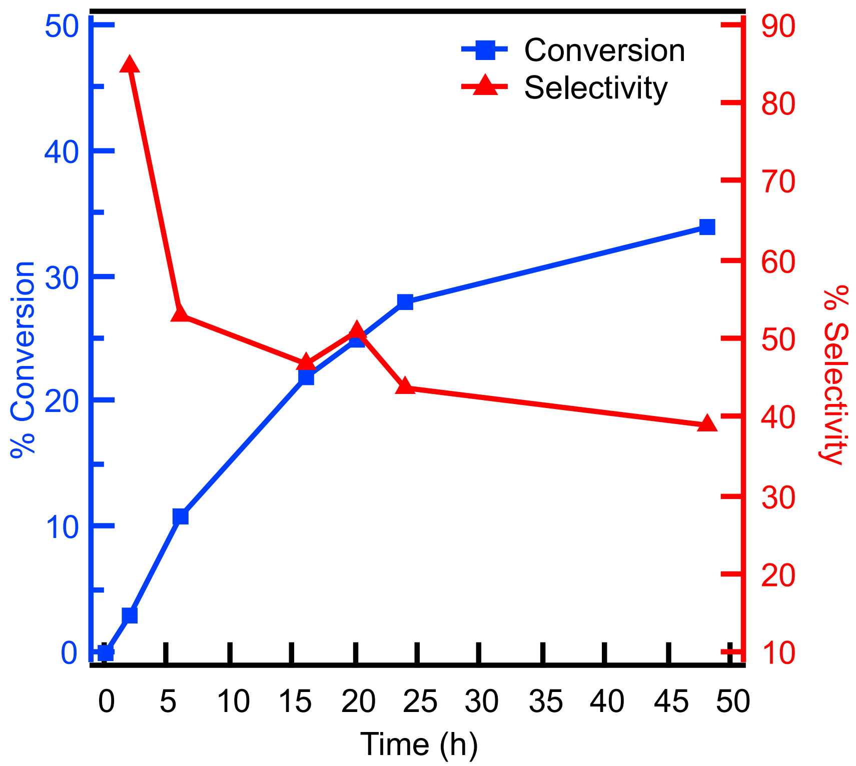


Figure 2. Kinetic evaluation of IMO-R over 48 hours. Kinetic evaluation of IMO-R over 48 hours. Data points are collected at 2, 6, 16, 20, 24, and 48 hours. The test is performed using 100 mg of IMO at 100 °C with 1 g of 10 wt% glucose solution. The glucose conversion is in blue (left axis) and fructose selectivity is in red (right axis).

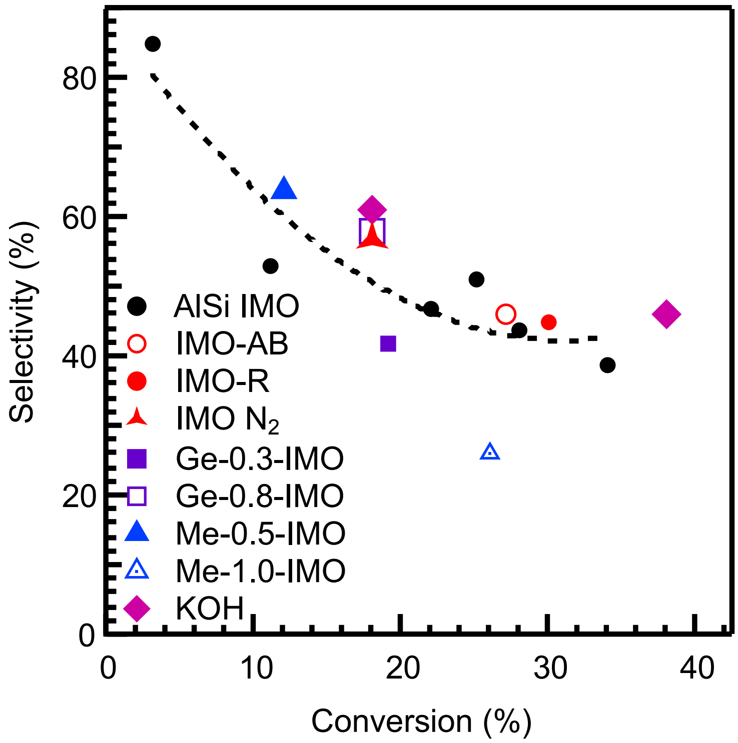


Figure 3. A comparison of the conversion and selectivity for different imogolite catalysts compared to KOH [33,34]. The reaction conditions are 100 mg of imogolite catalyst per 1 gram of a 10 wt% glucose solution in air at a reaction temperature of 100°C. IMO N_2 corresponds to using the IMO catalyst under nitrogen. For the IMO catalysts, a dashed line is plotted to show trend of conversion with increasing selectivity.

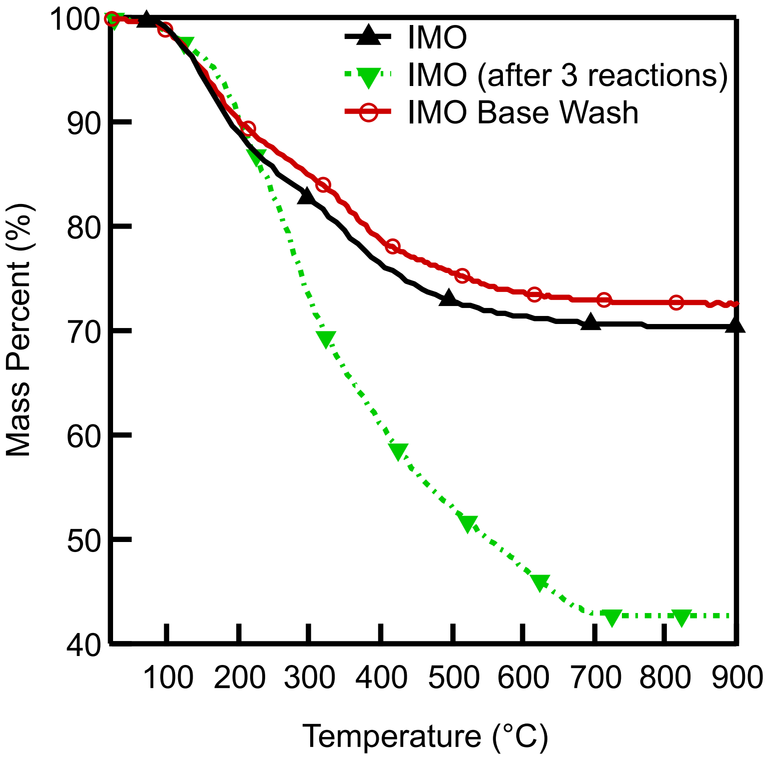


Figure 4. TGA mass percent curve of as-synthesized IMO (black), the recycled IMO after three reactions (green), and the IMO catalyst after washing with a 1 M NH_4OH solution (red).