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**Ammonia-treated metal oxides as base catalysts for selective  
isomerization of glucose in water**

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## 1 **Abstract**

2 Various metal oxides (MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and CeO<sub>2</sub>) were treated with  
3 NH<sub>3</sub> for incorporating nitrogen into the structure of metal oxides. The pristine and NH<sub>3</sub>-treated metal  
4 oxides were used as solid base catalysts for isomerization of glucose to fructose in water. SiO<sub>2</sub> and  
5 Nb<sub>2</sub>O<sub>5</sub> showed a large increment of nitrogen content by the treatment with NH<sub>3</sub>. FT-IR study on NH<sub>3</sub>-  
6 treated SiO<sub>2</sub> revealed that NH<sub>3</sub> reacted with terminal silanol groups and siloxane bonds to form Si-  
7 NH<sub>2</sub> and Si-NH-Si groups. Meanwhile, nitrogen was incorporated into bulk crystal of Nb<sub>2</sub>O<sub>5</sub>, causing  
8 amorphization of the crystal. Of all the samples, pristine and NH<sub>3</sub>-treated MgO showed highest  
9 catalytic activity for the isomerization of glucose. However, the selectivity to fructose was low due  
10 to subsequent reactions of formed fructose. Catalytic activity of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> was increased by the  
11 treatment with NH<sub>3</sub>, while that of the other metal oxides was not affected. Particularly, the catalytic  
12 activity of SiO<sub>2</sub> emerged after the treatment with NH<sub>3</sub> and was enhanced by increasing the  
13 temperature for the treatment up to 800 °C. While fructose was consumed by subsequent reactions  
14 over MgO, decreasing the selectivity, such reactions of fructose were not noticeable over NH<sub>3</sub>-treated  
15 SiO<sub>2</sub>. Consequently, NH<sub>3</sub>-treated SiO<sub>2</sub> showed higher selectivity to fructose and gave higher carbon  
16 balance than MgO.

17

18

19 **Keywords:** Fructose; Glucose; Isomerization; Knoevenagel condensation; Oxynitride; Solid base

## 1 **1. Introduction**

2 Biomass is expected to be a carbon source for production of chemicals in the future. Since cellulose  
3 is the major component in lignocellulosic plant biomass, glucose is an important intermediate material  
4 for the production of chemicals from biomass. With a view to manufacturing useful chemicals from  
5 biomass, fructose is considered to be more preferable than glucose. For instance, the production of 5-  
6 hydroxymethylfurfural (HMF), which is a potential precursor for bio-based furanics, has been  
7 achieved in acceptable yield from fructose, though the production of HMF from glucose is much  
8 more difficult and still a challenging issue [1-5]. Thus, isomerization of glucose to fructose is a  
9 primary reaction to utilize biomass as a feedstock for chemicals [6,7].

10 The first example of a chemocatalyst for the isomerization of saccharides was base catalysts  
11 found by Lobry de Bruyn and van Ekenstein in 19<sup>th</sup> century. Since their pioneering research,  
12 classically, various types of homogeneous base catalysts were investigated as catalysts [8,9].  
13 However, with concern over the problems arising from the use of homogenous base catalysts,  
14 research attention has been paid to heterogeneous base catalysts. So far, diverse materials such as  
15 single metal oxides [10-13], hydrotalcite [14-18], zeotype materials [18-21], metallosilicate [22],  
16 polymer-based materials [23,24] and supported amine (imine) [25,26] have been studied as solid base  
17 catalysts.

18 From the viewpoint of availability, handling, and cost, basic single metal oxides such as  
19 MgO and ZrO<sub>2</sub> have been expected to be promising candidates as catalysts for the isomerization of  
20 glucose to fructose. However, the use of these metal oxides resulted in low selectivity to fructose and

1 occasionally significant loss of carbon balance [11,13,17]. Hence, modification of such metal oxides  
2 is absolutely indispensable to improve the selectivity to fructose.

3 Treatment of metal oxides with  $\text{NH}_3$  at high temperature is a well-known method to  
4 incorporate nitrogen into metal oxides and modify their properties. Many examples of the treatment  
5 are found in silicon-based materials such as amorphous silica [27,28], mesoporous silica [29,30], and  
6 aluminosilicates including zeolites [30-33]. Due to the incorporation of nitrogen onto their surface by  
7 the treatment, these materials gained base properties and were usable as solid base catalysts [27-32].  
8 However, to our knowledge, there has never been a report on application of such  $\text{NH}_3$ -treated metal  
9 oxides as solid base catalysts for the isomerization of saccharides.

10 In the present study, catalytic properties of various pristine and  $\text{NH}_3$ -treated metal oxides  
11 were investigated in the isomerization of glucose to fructose. We found that  $\text{NH}_3$ -treated  $\text{SiO}_2$  with  
12 preferable base properties promoted the isomerization of glucose selectively.

13

## 14 **2. Experimental**

### 15 *2.1. Materials.*

16 Benzaldehyde (98%), 1,4-dioxane (99.5%), ethyl cyanoacetate (98%), fructose (99%),  
17 glucose (98%), octane (98%), and toluene (99.5%) were purchased from Wako Pure Chemical. He  
18 (99.99%) and  $\text{NH}_3$  (99.9%) were purchased from Air Water Inc.

19  $\text{TiO}_2$  (STR-100N) was purchased from Sakai Chemical Industry.  $\text{ZrO}_2$  (RC-100), and  $\text{CeO}_2$   
20 (type A) were purchased from Daiichi Kigenso Kagakukogyo.  $\text{Al}_2\text{O}_3$  (AEROXIDE Alu C) and  $\text{SiO}_2$

1 (Aerosil 300) were kindly given by Nippon Aerosil. MgO (500A) and Nb<sub>2</sub>O<sub>5</sub> hydrate made by UBE  
2 Material Industries and CBMM, respectively, were obtained through the Japan Reference Catalyst  
3 Project, Catalysis Society of Japan.

4

### 5 *2.2. Treatment of metal oxides with NH<sub>3</sub>.*

6 MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and CeO<sub>2</sub> were tested as catalysts for isomerization  
7 of saccharides. Prior to the use, all the powdery metal oxides were calcined in air at 500 °C for 5 h  
8 using a muffle furnace. The calcined metal oxides were pressed, crushed and sieved into 500 – 710  
9 μm in size. The sieved sample was placed in the middle of a quartz tube and sandwiched with quartz  
10 wool at both sides. By using a horizontal tubular electric furnace, the sample was treated in NH<sub>3</sub> flow  
11 (20 mL/min for 1 g of metal oxide) at 500 °C for 5 h and then purged with He flow at the same flow  
12 rate at 500 °C for 0.5 h. After cooled down to ambient temperature in He flow, the sample was taken  
13 out and ground. The powdery sample was used for characterization and catalytic reactions. The  
14 samples treated with NH<sub>3</sub> are denoted with -N at the end of the name of the metal oxides, e.g., MgO-  
15 N. The treatment with NH<sub>3</sub> was conducted at 600, 700, and 800 °C in the same manner as that at 500  
16 °C. These samples are denoted with the temperature at the end of the name, e.g., SiO<sub>2</sub>-N800.

17

### 18 *2.3. Characterization.*

19 Powder XRD patterns were collected using Cu K $\alpha$  radiation (30 kV, 15 mA) on a Rigaku  
20 MiniFlex diffractometer. Nitrogen content of the samples was determined by CHN analysis using a

1 vario MICRO cube elemental analyzer (elementar). N<sub>2</sub> adsorption isotherms were measured using a  
2 BEL-mini analyzer (MicrotracBEL) at -196 °C. Prior to the measurements, powder samples were  
3 pretreated in N<sub>2</sub> flow at 300 °C for 1 h. Specific surface area was calculated by the Brunauer–Emmett–  
4 Teller (BET) method.

5 Base properties of the samples were examined by temperature-programmed desorption of  
6 carbon dioxide (CO<sub>2</sub>-TPD) using a BEL-TPD analyzer (MicrotracBEL) equipped with a quadrupole  
7 mass spectrometer M-QA100F (ANELVA). A powder sample (50 mg) was pretreated at 500 °C for 1  
8 h in He flow (20 mL/min). After cooled down to 50 °C in He flow, the sample was exposed to CO<sub>2</sub>  
9 (27 kPa) for 10 min. The sample was purged with He flow (20 mL/min) at the same temperature for  
10 0.5 h to remove weakly adsorbed CO<sub>2</sub>. A TPD profile was obtained by increasing the temperature of  
11 the sample from 50 to 500 °C at the rate of 10 °C/min in He flow (20 mL/min) and concentration of  
12 CO<sub>2</sub> (m/z = 44) in the effluent gas was monitored by the quadrupole mass spectrometer.

13 FT-IR spectra were measured on JASCO FTIR-4600. A powder sample (50 mg) was  
14 pelletized to a self-supporting disk and set in a quartz cell connected to a vacuum line. The sample  
15 was heated to 400 °C and kept for 1 h *in vacuo* as a pretreatment. A spectrum was recorded at ambient  
16 temperature.

17

#### 18 2.4. Isomerization of glucose.

19 Catalytic performance of pristine and NH<sub>3</sub>-treated metal oxides was evaluated in  
20 isomerization of glucose to fructose in water (Scheme 1). A powder catalyst (50 mg) was added to 5

1 mL of aqueous solution of glucose (50 mM) in a test tube. The suspension was heated at 80 °C using  
2 an aluminum block heater. After a pre-set time, the reaction was quenched by cooling the test tube in  
3 an ice bath. The solid sample was removed with a membrane filter and the resulting filtrate was  
4 analyzed on an HPLC using an LC-20A (SHIMADZU) equipped with an ion-exclusion column  
5 (ROA-Organic Acid, Phenomenex). Glucose and products in the filtrate solution were detected with  
6 a refractive index detector and their amount was calculated according to the calibration curves with  
7 1,4-dioxane as an internal standard.

8 To identify by-products, the filtrate was analyzed on a GC-MS (SHIMADZU GCMS-  
9 QP2010SE) equipped with a capillary column (SHIMADZU SH-Rxi-5Sil MS). In order to analyze  
10 non-volatile compounds such as glucose and fructose, trimethylsilylation was conducted. An aqueous  
11 solution of the filtrate (1 mL) was exposed to N<sub>2</sub> flow and evaporated to dryness. Then, 2 mL of  
12 pyridine was added as a solvent and 0.25 mL of 1-trimethylsilylimidazole was added and kept static  
13 for 0.5 h. The obtained pyridine solution was analyzed on the GC-MS and products were identified  
14 with reference to a database.

15

## 16 2.5. Knoevenagel condensation

17 Catalytic performance of the pristine and NH<sub>3</sub>-treated metal oxides was also evaluated in  
18 Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate to ethyl cyanocinnamate  
19 (Scheme 2). A powdery sample was added to the toluene solution of benzaldehyde and ethyl  
20 cyanoacetate in a test tube and the suspension was heated at 70 °C for 2 h using an aluminum block

1 heater. The solid samples were removed by centrifugation and the supernatant was analyzed by GC-  
2 FID equipped with a ZB-1 column (30 m × 0.25 mm × 0.5 μm, Phenomenex).

3

### 4 **3. Results and discussion**

#### 5 *3.1. Composition and structure.*

6 Nitrogen content determined by CHN analysis is shown in Table 1. All the pristine metal  
7 oxides contained only a small amount of nitrogen below 20 μmol/g. The treatment of MgO, TiO<sub>2</sub>, and  
8 ZrO<sub>2</sub> with NH<sub>3</sub> resulted in only a small increment of the nitrogen content and the obtained samples  
9 had the nitrogen content less than 100 μmol/g. For Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, the nitrogen content was  
10 moderately increased to 130 and 230 μmol/g, respectively. A large increment of nitrogen was  
11 observed on Nb<sub>2</sub>O<sub>5</sub>-N, probably due to incorporation of nitrogen inside bulk crystal, which is  
12 explained later. When SiO<sub>2</sub> was treated at 500 °C, a moderate increment of nitrogen was found (210  
13 μmol/g for SiO<sub>2</sub>-N500). By increasing the temperature for the treatment, the nitrogen content was  
14 drastically increased up to 1140 μmol/g for SiO<sub>2</sub>-N800.

15 Figure 1 shows XRD patterns of the pristine and NH<sub>3</sub>-treated metal oxides. MgO and MgO-  
16 N showed diffraction patterns of the rock salt-type cubic structure, indicating that no significant  
17 change of the structure in the bulk occurred during the treatment with NH<sub>3</sub>. However, the intensities  
18 of diffraction lines became higher after the treatment because of crystallite growth, which was  
19 consistent with a small decrease in specific surface area (Table 1). Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>-N showed  
20 diffraction patterns typical to γ-Al<sub>2</sub>O<sub>3</sub>. SiO<sub>2</sub> showed only a halo peak around 20°, reflecting its

1 amorphous structure. Even after the treatment at 800 °C, SiO<sub>2</sub>-N800 retained the amorphous structure.  
2 TiO<sub>2</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub> had rutile, tetragonal, and cubic structures, respectively, and their structures  
3 were retained after the treatment with NH<sub>3</sub>. Nb<sub>2</sub>O<sub>5</sub> showed a diffraction pattern assigned to  
4 orthorhombic structure. After the treatment with NH<sub>3</sub>, similar diffraction lines were observed in lower  
5 intensity on undulated baseline, implying amorphization of the crystalline structure during the  
6 treatment. Considering that Nb<sub>2</sub>O<sub>5</sub>-N had a high nitrogen content, it is presumed that Nb<sub>2</sub>O<sub>5</sub> was  
7 highly reactive for NH<sub>3</sub> under the treatment conditions and that incorporation of a large amount of  
8 nitrogen inside the crystal induced the amorphization.

9 Base properties of the pristine and NH<sub>3</sub>-treated metal oxides were examined by CO<sub>2</sub>-TPD  
10 (Figure S1). MgO showed a broad desorption of CO<sub>2</sub> from 100 to 300 °C and the number of base  
11 sites was 40 μmol/g, which did not change significantly after the treatment with NH<sub>3</sub> (Table 1). ZrO<sub>2</sub>  
12 and ZrO<sub>2</sub>-N had a small number of base sites at ~20 μmol/g. CeO<sub>2</sub> and CeO<sub>2</sub>-N showed similar  
13 desorption peaks at ~100 °C, but the number of base sites was slightly decreased by the treatment  
14 with NH<sub>3</sub>. This is probably because a part of oxygen that originally formed base sites was consumed  
15 by the reaction with NH<sub>3</sub> and the resulting nitrogen sites did not adsorb CO<sub>2</sub>. The other pristine and  
16 NH<sub>3</sub>-treated metal oxides adsorbed only a negligible amount of CO<sub>2</sub>, independent of their nitrogen  
17 content.

18 MgO, ZrO<sub>2</sub>, and CeO<sub>2</sub> are known as basic metal oxides and in fact, each of these materials  
19 adsorbed a considerable amount of CO<sub>2</sub>. For these metal oxides, oxygen atoms with low coordination  
20 numbers can act as base sites that adsorb CO<sub>2</sub> [34]. Meanwhile, for all the metal oxides, nitrogen

1 atoms incorporated onto them had only weak affinity for CO<sub>2</sub> [35,36]. As a result, the increment of  
2 base sites by the treatment with NH<sub>3</sub> was negligible.

3

### 4 *3.2. Isomerization of glucose to fructose.*

5 Catalytic properties of the pristine and NH<sub>3</sub>-treated metal oxides were evaluated in the  
6 isomerization of glucose to fructose (Table 2). The isomerization hardly proceeded without a catalyst  
7 (Blank in Table 2). MgO showed high catalytic activity and achieved 52.2% conversion of glucose.  
8 However, selectivity to fructose was only 65.8% and yield of fructose was 34.4%. Following MgO,  
9 ZrO<sub>2</sub> showed high activity for the isomerization, giving 9.7% yield of fructose at 14.1% conversion  
10 of glucose. TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and CeO<sub>2</sub> showed poor catalytic activity and gave low yield of fructose less  
11 than 3%. Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> g were basically inactive for the isomerization.

12 MgO-N also showed high activity similar to that of MgO, but the selectivity to fructose was  
13 further decreased to 55.5%. In addition, the recovery of saccharides, which corresponds to the total  
14 amount of glucose and fructose after the reaction, was only 82.2% and 73.9% for MgO and MgO-N,  
15 respectively, indicating that unselective conversion of glucose occurred over these catalysts. The  
16 treatment with NH<sub>3</sub> was not effective for TiO<sub>2</sub>, ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and CeO<sub>2</sub> and their catalytic  
17 performance was altered only slightly by the treatment.

18 Catalytic activity of SiO<sub>2</sub> emerged after the treatment with NH<sub>3</sub>. SiO<sub>2</sub>-N500 gave 11.4%  
19 yield of fructose at 12.1% conversion of glucose. The activity was further increased by the treatment  
20 at 600 °C; SiO<sub>2</sub>-N600 gave 20.2% yield of fructose. Further increase in the temperature led to a slight

1 increase in the activity and eventually, SiO<sub>2</sub>-N800 gave 22.8% yield of fructose. It is noteworthy that  
2 NH<sub>3</sub>-treated SiO<sub>2</sub> catalysts showed high selectivity to fructose over 90% and that the saccharides  
3 recovery was nearly 100%, which was quite different to MgO-based ones. While Al<sub>2</sub>O<sub>3</sub> was inactive  
4 for the isomerization of glucose, Al<sub>2</sub>O<sub>3</sub>-N promoted the reaction and gave 7.2% yield of fructose.  
5 These results demonstrated that the treatment with NH<sub>3</sub> was effective for SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> to enhance  
6 their activity and that the isomerization occurred over nitrogen incorporated onto these materials.

7  
8 *3.3. Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.*

9 We applied Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate to ethyl  
10 cyanocinnamate as a typical base-catalyzed reaction for evaluating catalytic properties of the pristine  
11 and NH<sub>3</sub>-treated metal oxides (Figure 2). Only MgO showed catalytic activity for the reaction among  
12 the pristine metal oxides. For almost all the metal oxides except for Nb<sub>2</sub>O<sub>5</sub>, the catalytic activity  
13 appeared obviously after the treatment with NH<sub>3</sub>. Especially, NH<sub>3</sub>-treated SiO<sub>2</sub> samples showed high  
14 catalytic activity due to the plenty of nitrogen incorporated on them. SiO<sub>2</sub>-N500 gave 11% yield of  
15 ethyl cyanocinnamate and SiO<sub>2</sub>-N600 showed higher activity, achieving 46% yield. SiO<sub>2</sub>-N700 and  
16 -N800 samples gave slightly higher yield than SiO<sub>2</sub>-N600. This trend in the catalytic activity for the  
17 Knoevenagel condensation was similar to that observed in the isomerization of glucose. Presumably,  
18 these two reactions are promoted by the same active nitrogen sites. Al<sub>2</sub>O<sub>3</sub>-N and ZrO<sub>2</sub>-N, which had  
19 similar nitrogen content, showed similar moderate catalytic activity and gave ~9% yield of the  
20 product. Although having the relatively large nitrogen content, CeO<sub>2</sub>-N gave only 5% yield of the

1 product. TiO<sub>2</sub>-N having a small nitrogen content gave 7% yield of the product. In spite of the large  
2 nitrogen content, Nb<sub>2</sub>O<sub>5</sub>-N was inactive for the Knoevenagel condensation nor the isomerization of  
3 glucose. Since nitrogen was incorporated into the bulk crystal of Nb<sub>2</sub>O<sub>5</sub>, as observed in the  
4 amorphization by XRD, such nitrogen did not contribute to the catalysis on the surface of the crystal.

5

#### 6 *3.4. Formation of active nitrogen base sites on SiO<sub>2</sub>.*

7 The treatment with NH<sub>3</sub> was effective to enhance the catalytic activity of particular metal  
8 oxides such as SiO<sub>2</sub> for both isomerization of glucose and Knoevenagel condensation. Meanwhile,  
9 TiO<sub>2</sub> and CeO<sub>2</sub> showed poor catalytic activity after the treatment with NH<sub>3</sub>. The catalytic activity of  
10 NH<sub>3</sub>-treated metal oxides was presumably related to the structure of surface nitrogen species. Hence,  
11 choosing SiO<sub>2</sub> and CeO<sub>2</sub> as representative samples, the structure of nitrogen was examined by  
12 measuring IR spectra of the pristine and NH<sub>3</sub>-treated samples (Figure 3A). In a spectrum of SiO<sub>2</sub>, a  
13 sharp absorption band for O-H stretching vibration of terminal silanol appeared at ~3740 cm<sup>-1</sup> on a  
14 broad band for hydrogen-bonded silanol groups at 3500 – 3800 cm<sup>-1</sup>. For NH<sub>3</sub>-treated SiO<sub>2</sub> samples,  
15 the intensity of the band for terminal silanol was decreased, but absorption bands of N-H stretching  
16 vibration were newly observed at 3350 – 3450 cm<sup>-1</sup> [37,38]. Obviously, terminal silanol reacted with  
17 NH<sub>3</sub> to form surface NH<sub>x</sub> groups. In contrast, such absorption bands for O-H and N-H stretching  
18 vibrations were hardly observed for CeO<sub>2</sub> nor CeO<sub>2</sub>-N. Since CeO<sub>2</sub> had only a small amount of  
19 terminal hydroxyl groups, CeO<sub>2</sub>-N had only a limited amount of surface NH<sub>x</sub> groups if terminal  
20 hydroxyl groups reacted with NH<sub>3</sub> and consequently showed the poor catalytic activity.

1           The changes of functional groups on SiO<sub>2</sub> were clearly observed in difference IR spectra  
2 (Figure 3B). After the treatment with NH<sub>3</sub> at 500 °C, the absorption band for terminal silanol at 3736  
3 cm<sup>-1</sup> was slightly decreased, but a broad band for hydrogen-bonded silanol at 3600 – 3700 cm<sup>-1</sup> was  
4 increased. Additionally, an absorption band for Si-NH<sub>2</sub> appeared at 3417 cm<sup>-1</sup>. By the treatment at  
5 600 °C, the absorption band for Si-NH<sub>2</sub> was increased. Upon increasing the temperature to 700 and  
6 800 °C, absorption bands for Si-NH-Si were observed at 3377 and 3437 cm<sup>-1</sup> in high intensities. At  
7 600 °C or higher, terminal and hydrogen-bonded silanols were decreased and finally at 800 °C,  
8 hydrogen-bonded silanol was largely decreased, compared to SiO<sub>2</sub>. Based on the above observation,  
9 a plausible scheme for the formation of NH<sub>x</sub> groups on SiO<sub>2</sub> is described in Scheme 3. Below 600 °C,  
10 NH<sub>3</sub> reacted with terminal silanol to form Si-NH<sub>2</sub>, releasing H<sub>2</sub>O. In addition, NH<sub>3</sub> cleaved Si-O-Si  
11 bond to form Si-NH<sub>2</sub> and silanol. At further elevated temperatures, condensation of surface functional  
12 groups dominantly occurred to form Si-NH-Si and regenerate Si-O-Si bonds.

13           Catalytic activity of SiO<sub>2</sub> was significantly enhanced by the treatment with NH<sub>3</sub> at 500 °C  
14 and increased more by the treatment at 600 °C. However, further increase in the temperature to 700  
15 and 800 °C resulted in only a small increase in the activity. This trend well agrees with the change in  
16 the intensity of the absorption band for Si-NH<sub>2</sub> at 3417 cm<sup>-1</sup>, indicating that a catalytically active  
17 nitrogen site is Si-NH<sub>2</sub> rather than Si-NH-Si.

18  
19 *3.4. Difference in catalytic performance between SiO<sub>2</sub>-N800 and MgO.*

20           The catalytic performance of SiO<sub>2</sub>-N800 was compared with that of MgO in detail in the

1 time course of the isomerization of glucose (Figure 4). In the presence of SiO<sub>2</sub>-N800, the conversion  
2 of glucose reached plateau at ~40%. Since the isomerization of glucose to fructose is a reversible  
3 reaction and glucose is thermodynamically favorable under the reaction conditions, the conversion of  
4 glucose seemed to level off in long-term reactions unless side reactions proceeded. In contrast, the  
5 conversion of glucose constantly increased as time went by in the presence of MgO. The selectivity  
6 to fructose was decreased as the conversion was increased, suggesting that fructose was consumed  
7 by subsequent reactions. Since such subsequent reactions consumed a part of formed fructose and  
8 consequently, the reaction did not reach the chemical equilibrium between glucose and fructose, the  
9 conversion of glucose constantly increased. Therefore, SiO<sub>2</sub>-N800 was found to be more suitable than  
10 MgO as a catalyst for the isomerization of glucose in terms of selectivity to fructose.

11 Catalytic performance was further compared between SiO<sub>2</sub>-N800 and MgO for  
12 isomerization reaction using fructose as a reactant instead of glucose (Figure 5). Since fructose is  
13 generally more reactive than glucose, the catalyst dosage for the isomerization of fructose was only  
14 a half of that for glucose. For SiO<sub>2</sub>-N800, the conversion of fructose was slightly higher than the yield  
15 of glucose at any reaction time, implying the high selectivity to glucose (Figure 5a). In the presence  
16 of MgO, while fructose was rapidly consumed and the conversion of fructose reached 50% within 1  
17 h, the maximum yield of glucose was below 20% (Figure 5b). Although several by-products such  
18 as dihydroxyacetone and glyceraldehyde were identified by analysis on a GC-MS (Figure S2), total  
19 yield of them did not possibly account for the difference between the conversion of fructose and the  
20 yield of glucose for the reaction with MgO. Colorless solution of fructose colored in the course of

1 reaction in the presence of MgO. After 5 h, the solution became dark brown due to the formation of  
2 colored by-products. Formation of such colored by-products was the main cause of the low selectivity  
3 to glucose. Similar phenomena was also observed in the isomerization of glucose to fructose. In the  
4 isomerization of glucose, the rapid subsequent reactions of fructose would lead to the low selectivity  
5 to fructose.

6 Table 3 summarizes reaction results on the isomerization of glucose and fructose over SiO<sub>2</sub>-  
7 N800 and MgO. For both saccharides, MgO gave higher conversion and higher yield of the desired  
8 product. However, in the cases using MgO, the saccharides recovery was low, especially in the  
9 isomerization of fructose due to the unselective reactions of fructose. Comparing the reactivity,  
10 fructose was much more reactive than glucose over MgO, while both saccharides showed similar  
11 reactivity over SiO<sub>2</sub>-N800. The high reactivity of fructose over MgO could make it impossible to  
12 produce fructose selectively through the isomerization of glucose.

13 There was no clear correlation between the number of base sites determined by CO<sub>2</sub>-TPD  
14 and the catalytic activity for the isomerization nor Knoevenagel condensation. Contrary to MgO,  
15 ZrO<sub>2</sub>, and CeO<sub>2</sub>, which adsorbed a large amount of CO<sub>2</sub>, NH<sub>3</sub>-treated metal oxides including SiO<sub>2</sub>-  
16 based samples hardly adsorbed CO<sub>2</sub>, though they showed catalytic activity for Knoevenagel  
17 condensation. Additionally, while MgO promoted the reaction of fructose more than that of glucose,  
18 SiO<sub>2</sub>-N800 promoted the reactions of both saccharides almost equally. These results suggest different  
19 base properties between oxygen sites on MgO and nitrogen sites on SiO<sub>2</sub>-N800.

20

### 1 3.5. Reaction mechanism for isomerization of saccharides over $\text{SiO}_2\text{-N800}$ .

2 In order to demonstrate that  $\text{SiO}_2\text{-N800}$  can act as a base catalyst for the isomerization of  
3 glucose, sulfuric acid was added into the solution for the isomerization of glucose with  $\text{SiO}_2\text{-N800}$ .  
4 The presence of sulfuric acid strongly inhibited the isomerization of glucose, because the  
5 homogeneous acid strongly coordinated to base sites on  $\text{SiO}_2\text{-N800}$  and inhibited reaction with  
6 glucose. Furthermore, in order to demonstrate that  $\text{SiO}_2\text{-N800}$  worked as a heterogeneous catalyst for  
7 the isomerization of glucose, a hot filtration test was done (Figure 6). The yield of fructose was 9.5%  
8 at 1 h with  $\text{SiO}_2\text{-N800}$ . Then, the solid catalyst was removed by filtration and the reaction was proceed  
9 again for further 2 h. The yield of fructose was slightly increased to 11.4% by homogeneous catalysis.  
10 However,  $\text{SiO}_2\text{-N800}$  gave much higher yield of fructose (22.8%) at 3 h, demonstrating that the  
11 isomerization of glucose was promoted predominantly by heterogeneous catalysis of  $\text{SiO}_2\text{-N800}$ .  
12 These results surely confirmed that  $\text{SiO}_2\text{-N800}$  can promote the isomerization of saccharides in water  
13 as a solid base catalyst.

14 Two types of reaction mechanism have been known for the catalytic isomerization of glucose  
15 to fructose; one is a hydride transfer mechanism promoted by Lewis acid catalysts such as metal  
16 chlorides [39] and Lewis-acidic zeolites [40-42]. The other is proton abstraction mechanism in which  
17 base catalysts abstract proton at C-2 of glucose to form the enediol intermediate and the following  
18 keto-enol tautomerization produces fructose [43]. It is well known that Knoevenagel condensation  
19 proceeds via abstraction of proton from active methylene compounds such as ethyl cyanoacetate.  
20 Based on the good correlation between the activity for the isomerization of glucose and that for

1 Knoevenagel condensation, SiO<sub>2</sub>-N800 as a base catalyst promoted the isomerization of glucose  
2 through the proton abstraction mechanism (Scheme 4).

3

### 4 *3.6. Reusability of SiO<sub>2</sub>-N800.*

5 In order to check the stability and reusability, the spent SiO<sub>2</sub>-N800 was recovered and used  
6 multiple times (Figure S3). After each reaction run, the solid catalyst was recovered by filtration,  
7 dried overnight at 60 °C, and reused in the next run. The yield of fructose was gradually decreased  
8 and eventually, for the fourth run, the yield of fructose was 7.4%. The nitrogen content of SiO<sub>2</sub>-N800  
9 was decreased from 1140 μmol/g to 500 μmol/g after the fourth run. The leaching of nitrogen during  
10 each reaction led to the decline in the catalytic activity. Future work needs to improve the stability of  
11 ammonia-treated metal oxides.

12

## 13 **4. Conclusions**

14 NH<sub>3</sub>-treated SiO<sub>2</sub> was found to deserve as a promising solid base catalyst for the  
15 isomerization of glucose to fructose in water. SiO<sub>2</sub>-N800 with the largest nitrogen content gave ~40%  
16 yield of fructose in ~90% selectivity, suppressing side reactions that lowered the selectivity to fructose.

17 Si-NH<sub>2</sub> was mainly formed by the treatment of SiO<sub>2</sub> with NH<sub>3</sub> at 500 – 600 °C and catalytic  
18 activity of SiO<sub>2</sub> was remarkably enhanced by the treatment with NH<sub>3</sub>. However, further increase in  
19 the temperature resulted in the formation of Si-NH-Si, leading to only a small increase in the activity.  
20 Si-NH<sub>2</sub> group was presumed to be a catalytically active nitrogen site on SiO<sub>2</sub>. Unlike MgO,

1 subsequent reactions of fructose was not considerable over NH<sub>3</sub>-treated SiO<sub>2</sub>, being more suitable  
2 than MgO as a catalyst for the isomerization of glucose in terms of selectivity to fructose.

3

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6

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**Table 1** Surface area, nitrogen content and basicity of pristine and NH<sub>3</sub>-treated metal oxides.

Sample	$S_{\text{BET}}^a$ (m <sup>2</sup> /g)	N content <sup>b</sup> ( $\mu\text{mol/g}$ )	Base site <sup>c</sup> ( $\mu\text{mol/g}$ )	Density (1/nm <sup>2</sup> )	
				Nitrogen	Base site
MgO	62	< 10	40	0.01	0.39
MgO-N	55	50	37	0.51	0.40
Al <sub>2</sub> O <sub>3</sub>	119	10	4	0.07	0.02
Al <sub>2</sub> O <sub>3</sub> -N	130	130	3	0.58	0.01
SiO <sub>2</sub>	378	10	5	0.02	< 0.01
SiO <sub>2</sub> -N500	353	210	2	0.36	< 0.01
SiO <sub>2</sub> -N600	373	350	2	0.57	< 0.01
SiO <sub>2</sub> -N700	382	700	2	1.10	< 0.01
SiO <sub>2</sub> -N800	363	1140	4	1.89	0.01
TiO <sub>2</sub>	58	20	9	0.21	0.09
TiO <sub>2</sub> -N	53	70	4	0.82	0.05
ZrO <sub>2</sub>	103	10	21	0.06	0.12
ZrO <sub>2</sub> -N	100	100	17	0.57	0.10
Nb <sub>2</sub> O <sub>5</sub>	66	20	4	0.18	0.04
Nb <sub>2</sub> O <sub>5</sub> -N	67	1060	5	9.56	0.04
CeO <sub>2</sub>	172	< 10	52	0.03	0.18
CeO <sub>2</sub> -N	164	230	40	0.83	0.15

<sup>a</sup> Specific surface area calculated by BET method.

<sup>b</sup> Content of nitrogen determined by CHN analysis.

<sup>c</sup> The number of base sites estimated by CO<sub>2</sub>-TPD.

**Table 2** Isomerization of glucose to fructose over pristine and NH<sub>3</sub>-treated metal oxides.

Catalyst	Conversion <sup>a</sup> (%)	Selectivity <sup>b</sup> (%)	Yield <sup>c</sup> (%)	Saccharides recovery <sup>d</sup> (%)
Blank	1.0	52.8	0.5	99.5
MgO	52.2	65.8	34.4	82.2
MgO-N	58.7	55.5	32.6	73.9
Al <sub>2</sub> O <sub>3</sub>	2.5	13.9	0.3	97.9
Al <sub>2</sub> O <sub>3</sub> -N	9.5	75.4	7.2	97.7
SiO <sub>2</sub>	1.5	43.4	0.6	99.2
SiO <sub>2</sub> -N500	12.1	94.5	11.4	99.3
SiO <sub>2</sub> -N600	21.3	94.5	20.2	98.8
SiO <sub>2</sub> -N700	22.9	91.4	20.9	98.0
SiO <sub>2</sub> -N800	25.0	91.3	22.8	97.8
TiO <sub>2</sub>	3.5	66.8	2.3	98.8
TiO <sub>2</sub> -N	5.8	75.5	4.4	98.6
ZrO <sub>2</sub>	14.1	69.1	9.7	95.6
ZrO <sub>2</sub> -N	10.8	88.9	9.6	98.8
Nb <sub>2</sub> O <sub>5</sub>	3.5	73.4	2.6	99.1
Nb <sub>2</sub> O <sub>5</sub> -N	1.4	85.5	1.2	99.8
CeO <sub>2</sub>	5.4	4.2	0.2	94.8
CeO <sub>2</sub> -N	6.7	3.6	0.2	93.6

Reaction conditions: Catalyst, 50 mg; Glucose, 0.25 mmol; Water, 5 mL; Temperature, 80 °C; Time, 3 h.

<sup>a</sup> Conversion of glucose.

<sup>b, c</sup> Selectivity to and yield of fructose, respectively.

<sup>d</sup> Total amount of glucose and fructose.

**Table 3** Catalytic performance of MgO and SiO<sub>2</sub>-N800 for isomerization of saccharides.

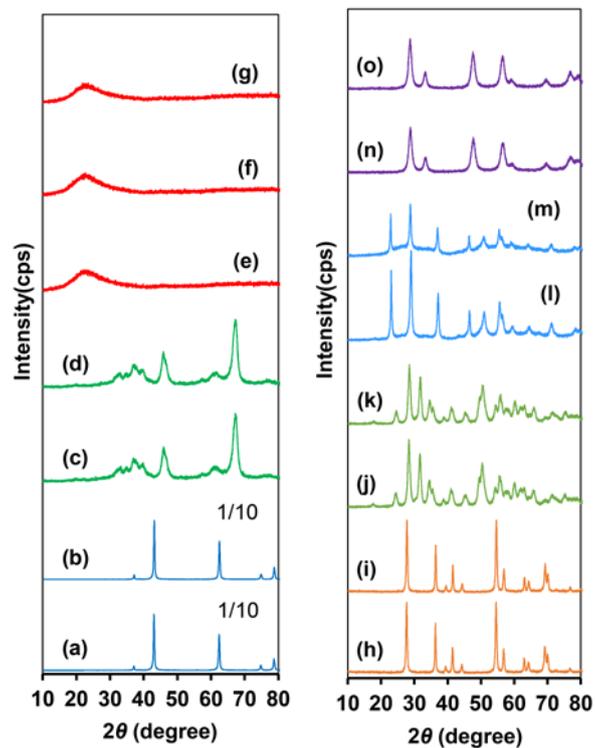
Catalyst	Substrate	Conversion <sup>a</sup> (%)	Yield <sup>b</sup> (%)	Saccharide recovery <sup>c</sup> (%)
MgO	Fructose	76.3	12.3	36.0
	Glucose	34.4	25.3	91.0
SiO <sub>2</sub> -N800	Fructose	8.8	8.7	99.9
	Glucose	10.1	9.5	99.4

Reaction conditions: Catalyst, 50 mg; Saccharide, 0.25 mmol; Water, 5 mL; Temperature, 80 °C; Time, 1 h.

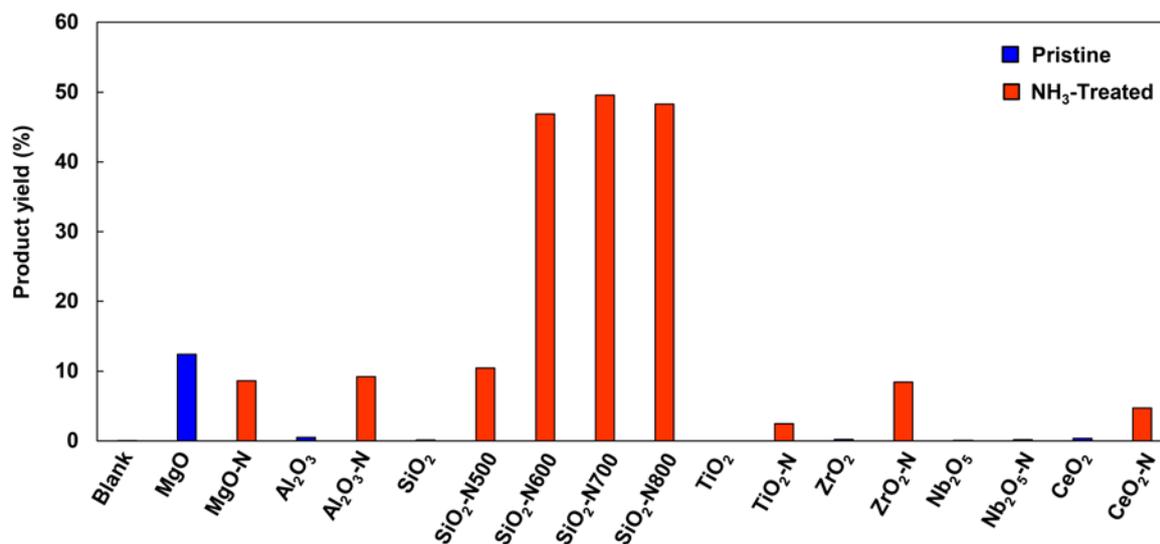
<sup>a</sup> Conversion of fructose or glucose.

<sup>b</sup> Yield of glucose or fructose.

<sup>c</sup> Total amount of glucose and fructose.

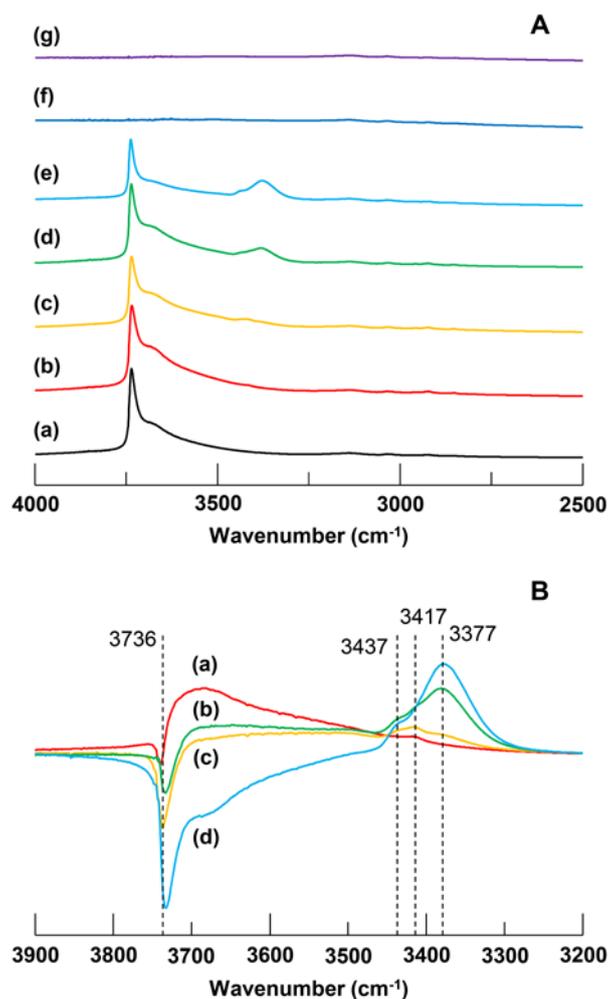


**Figure 1** XRD patterns of (a) MgO, (b) MgO-N, (c) Al<sub>2</sub>O<sub>3</sub>, (d) Al<sub>2</sub>O<sub>3</sub>-N, (e) SiO<sub>2</sub>, (f) SiO<sub>2</sub>-N500, (g) SiO<sub>2</sub>-N800, (h) TiO<sub>2</sub>, (i) TiO<sub>2</sub>-N, (j) ZrO<sub>2</sub>, (k) ZrO<sub>2</sub>-N, (l) Nb<sub>2</sub>O<sub>5</sub>, (m) Nb<sub>2</sub>O<sub>5</sub>-N, (n) CeO<sub>2</sub>, and (o) CeO<sub>2</sub>-N.

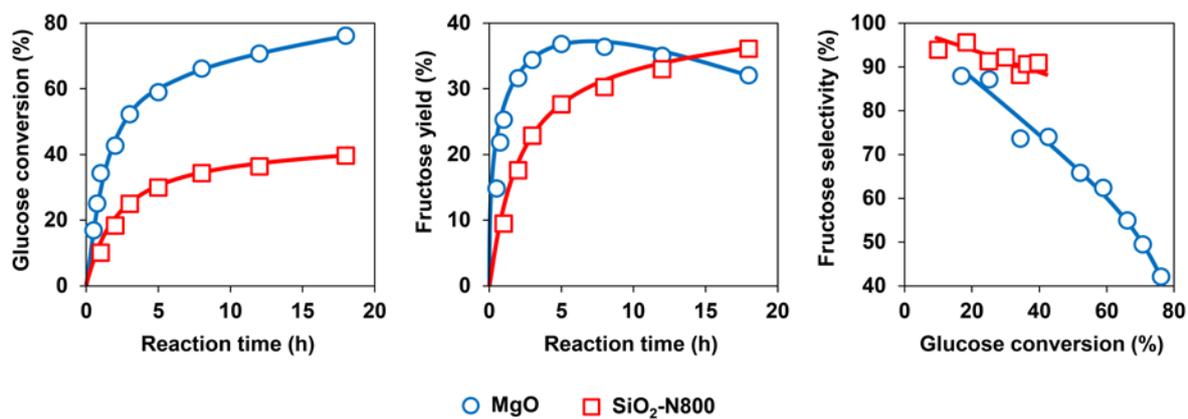


**Figure 2** Catalytic performance of pristine and NH<sub>3</sub>-treated metal oxides for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

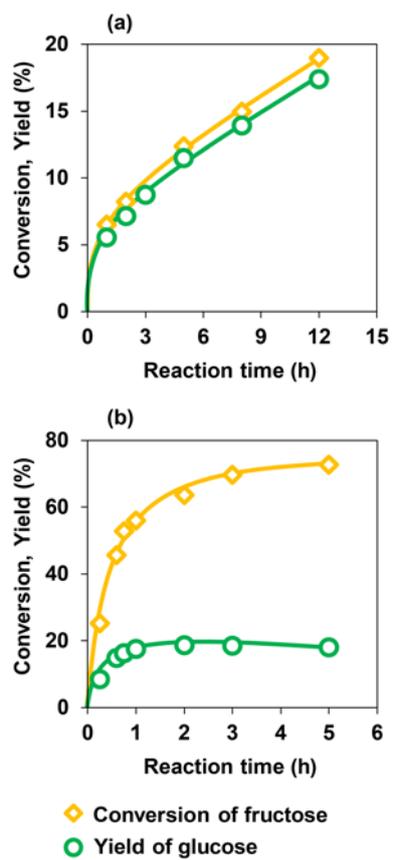
Reaction conditions: Catalyst, 25 mg; Benzaldehyde, 2.5 mmol; Ethyl cyanoacetate, 2.5 mmol; Toluene 2.5 mL; Temperature, 70 °C; Time, 2 h.



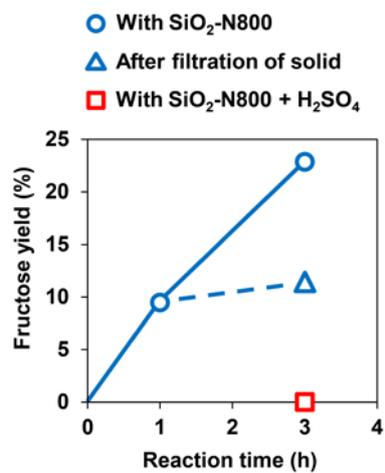
**Figure 3** A: IR spectra of (a) SiO<sub>2</sub>, (b) SiO<sub>2</sub>-N500, (c) SiO<sub>2</sub>-N600, (d) SiO<sub>2</sub>-N700, (e) SiO<sub>2</sub>-N800, (f) CeO<sub>2</sub>, and (g) CeO<sub>2</sub>-N. B: Difference spectra of (a) SiO<sub>2</sub>-N500, (b) SiO<sub>2</sub>-N600, (c) SiO<sub>2</sub>-N700, and (d) SiO<sub>2</sub>-N800 obtained by subtracting from the spectrum of SiO<sub>2</sub>.



**Figure 4** Isomerization of glucose to fructose over MgO and SiO<sub>2</sub>-N800 catalysts. Reaction conditions: Catalyst, 50 mg; Glucose, 0.25 mmol; Water, 5 mL; Temperature, 80 °C.

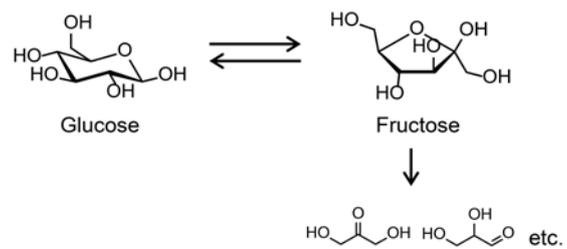


**Figure 5** Isomerization of fructose to glucose over (a) SiO<sub>2</sub>-N800 and (b) MgO catalysts. Reaction conditions: Catalyst, 25 mg; Fructose, 0.25 mmol; Water, 5 mL; Temperature, 80 °C.

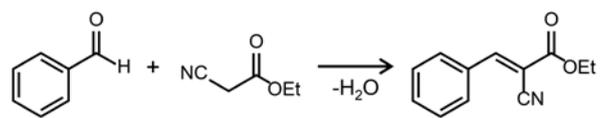


**Figure 6** Influence of removal of the catalyst or addition of sulfuric acid on isomerization of glucose over SiO<sub>2</sub>-N800.

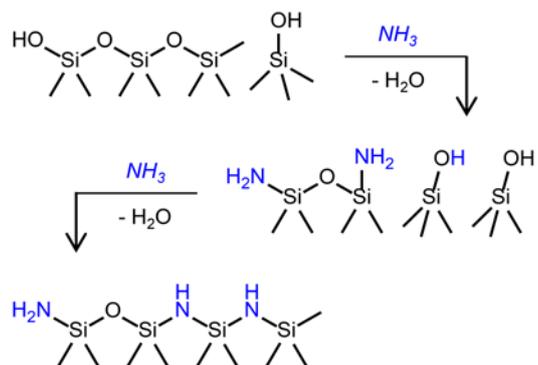
Reaction conditions: SiO<sub>2</sub>-N800, 50 mg; Glucose, 0.25 mmol; Water, 5 mL; H<sub>2</sub>SO<sub>4</sub>, 0 or 0.1 mmol; Temperature, 80 °C.



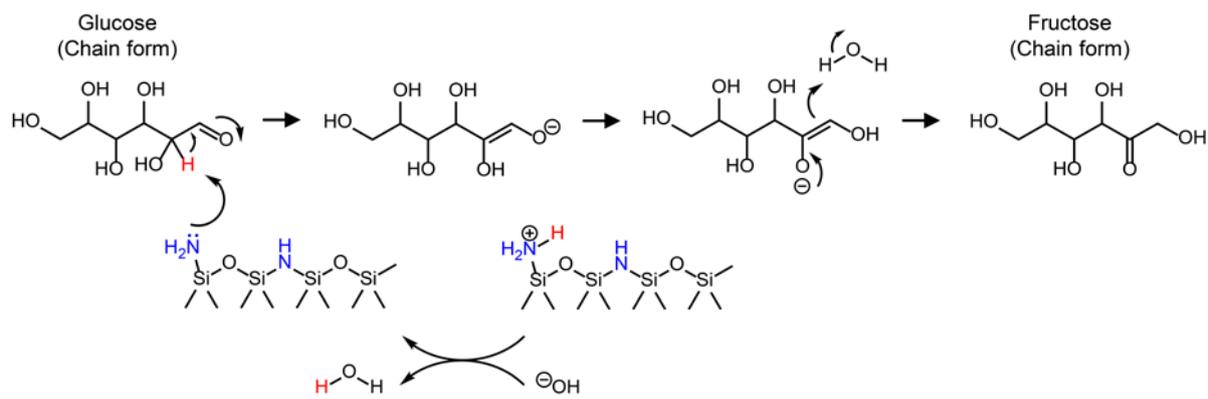
**Scheme 1** Reaction pathways for isomerization of saccharides.



**Scheme 2** Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.



**Scheme 3** Formation of Si-NH<sub>x</sub> groups on SiO<sub>2</sub>.



**Scheme 4** Plausible reaction mechanism for isomerization of saccharides over  $\text{NH}_3$ -treated  $\text{SiO}_2$ .