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3 **Ammonia-treated metal oxides as base catalysts for selective**

4 **isomerization of glucose in water**

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1 **Abstract**

2 Various metal oxides (MgO, Al₂O₃, SiO₂, TiO₂, ZrO₂, Nb₂O₅, and CeO₂) were treated with
3 NH₃ for incorporating nitrogen into the structure of metal oxides. The pristine and NH₃-treated metal
4 oxides were used as solid base catalysts for isomerization of glucose to fructose in water. SiO₂ and
5 Nb₂O₅ showed a large increment of nitrogen content by the treatment with NH₃. FT-IR study on NH₃-
6 treated SiO₂ revealed that NH₃ reacted with terminal silanol groups and siloxane bonds to form Si-
7 NH₂ and Si-NH-Si groups. Meanwhile, nitrogen was incorporated into bulk crystal of Nb₂O₅, causing
8 amorphization of the crystal. Of all the samples, pristine and NH₃-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 Al₂O₃ and SiO₂ was increased by the
11 treatment with NH₃, while that of the other metal oxides was not affected. Particularly, the catalytic
12 activity of SiO₂ emerged after the treatment with NH₃ 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 NH₃-treated
15 SiO₂. Consequently, NH₃-treated SiO₂ showed higher selectivity to fructose and gave higher carbon
16 balance than MgO.

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18

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

1. Introduction

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

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

From the viewpoint of availability, handling, and cost, basic single metal oxides such as MgO and ZrO₂ have been expected to be promising candidates as catalysts for the isomerization of 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 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 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 NH_3 -treated metal oxides
11 were investigated in the isomerization of glucose to fructose. We found that NH_3 -treated 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 NH_3 (99.9%) were purchased from Air Water Inc.

19 TiO_2 (STR-100N) was purchased from Sakai Chemical Industry. ZrO_2 (RC-100), and CeO_2
20 (type A) were purchased from Daiichi Kigenso Kagakukogyo. Al_2O_3 (AEROXIDE Alu C) and SiO_2

1 (Aerosil 300) were kindly given by Nippon Aerosil. MgO (500A) and Nb₂O₅ 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 NH₃.

6 MgO, Al₂O₃, SiO₂, TiO₂, ZrO₂, Nb₂O₅, and CeO₂ 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 NH₃ 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 NH₃ are denoted with -N at the end of the name of the metal oxides, e.g., MgO-
15 N. The treatment with NH₃ 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., SiO₂-N800.

17

18 2.3. Characterization.

19 Powder XRD patterns were collected using Cu Kα 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). N₂ adsorption isotherms were measured using a
2 BEL-mini analyzer (MicrotracBEL) at -196 °C. Prior to the measurements, powder samples were
3 pretreated in N₂ 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 (CO₂-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 CO₂
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 CO₂. 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 CO₂ (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 NH₃-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 N₂ 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 NH₃-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, TiO₂, and
8 ZrO₂ with NH₃ 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 Al₂O₃ and CeO₂, the nitrogen content was
10 moderately increased to 130 and 230 μmol/g, respectively. A large increment of nitrogen was
11 observed on Nb₂O₅-N, probably due to incorporation of nitrogen inside bulk crystal, which is
12 explained later. When SiO₂ was treated at 500 °C, a moderate increment of nitrogen was found (210
13 μmol/g for SiO₂-N500). By increasing the temperature for the treatment, the nitrogen content was
14 drastically increased up to 1140 μmol/g for SiO₂-N800.

15 Figure 1 shows XRD patterns of the pristine and NH₃-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 NH₃. 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). Al₂O₃ and Al₂O₃-N showed
20 diffraction patterns typical to γ-Al₂O₃. SiO₂ showed only a halo peak around 20°, reflecting its

1 amorphous structure. Even after the treatment at 800 °C, SiO₂-N800 retained the amorphous structure.
2 TiO₂, ZrO₂, and CeO₂ had rutile, tetragonal, and cubic structures, respectively, and their structures
3 were retained after the treatment with NH₃. Nb₂O₅ showed a diffraction pattern assigned to
4 orthorhombic structure. After the treatment with NH₃, similar diffraction lines were observed in lower
5 intensity on undulated baseline, implying amorphization of the crystalline structure during the
6 treatment. Considering that Nb₂O₅-N had a high nitrogen content, it is presumed that Nb₂O₅ was
7 highly reactive for NH₃ 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 NH₃-treated metal oxides were examined by CO₂-TPD
10 (Figure S1). MgO showed a broad desorption of CO₂ 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 NH₃ (Table 1). ZrO₂
12 and ZrO₂-N had a small number of base sites at ~20 μmol/g. CeO₂ and CeO₂-N showed similar
13 desorption peaks at ~100 °C, but the number of base sites was slightly decreased by the treatment
14 with NH₃. This is probably because a part of oxygen that originally formed base sites was consumed
15 by the reaction with NH₃ and the resulting nitrogen sites did not adsorb CO₂. The other pristine and
16 NH₃-treated metal oxides adsorbed only a negligible amount of CO₂, independent of their nitrogen
17 content.

18 MgO, ZrO₂, and CeO₂ are known as basic metal oxides and in fact, each of these materials
19 adsorbed a considerable amount of CO₂. For these metal oxides, oxygen atoms with low coordination
20 numbers can act as base sites that adsorb CO₂ [34]. Meanwhile, for all the metal oxides, nitrogen

1 atoms incorporated onto them had only weak affinity for CO₂ [35,36]. As a result, the increment of
2 base sites by the treatment with NH₃ was negligible.

3

4 3.2. *Isomerization of glucose to fructose.*

5 Catalytic properties of the pristine and NH₃-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 ZrO₂ showed high activity for the isomerization, giving 9.7% yield of fructose at 14.1% conversion
10 of glucose. TiO₂, Nb₂O₅, and CeO₂ showed poor catalytic activity and gave low yield of fructose less
11 than 3%. Al₂O₃ and SiO₂ 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 NH₃ was not effective for TiO₂, ZrO₂, Nb₂O₅, and CeO₂ and their catalytic
17 performance was altered only slightly by the treatment.

18 Catalytic activity of SiO₂ emerged after the treatment with NH₃. SiO₂-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; SiO₂-N600 gave 20.2% yield of fructose. Further increase in the temperature led to a slight

1 increase in the activity and eventually, SiO₂-N800 gave 22.8% yield of fructose. It is noteworthy that
2 NH₃-treated SiO₂ 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 Al₂O₃ was inactive
4 for the isomerization of glucose, Al₂O₃-N promoted the reaction and gave 7.2% yield of fructose.
5 These results demonstrated that the treatment with NH₃ was effective for SiO₂ and Al₂O₃ to enhance
6 their activity and that the isomerization occurred over nitrogen incorporated onto these materials.

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 NH₃-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 Nb₂O₅, the catalytic activity
13 appeared obviously after the treatment with NH₃. Especially, NH₃-treated SiO₂ samples showed high
14 catalytic activity due to the plenty of nitrogen incorporated on them. SiO₂-N500 gave 11% yield of
15 ethyl cyanocinnamate and SiO₂-N600 showed higher activity, achieving 46% yield. SiO₂-N700 and
16 -N800 samples gave slightly higher yield than SiO₂-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. Al₂O₃-N and ZrO₂-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, CeO₂-N gave only 5% yield of the

1 product. $\text{TiO}_2\text{-N}$ having a small nitrogen content gave 7% yield of the product. In spite of the large
2 nitrogen content, $\text{Nb}_2\text{O}_5\text{-N}$ was inactive for the Knoevenagel condensation nor the isomerization of
3 glucose. Since nitrogen was incorporated into the bulk crystal of Nb_2O_5 , as observed in the
4 amorphization by XRD, such nitrogen did not contribute to the catalysis on the surface of the crystal.

6 *3.4. Formation of active nitrogen base sites on SiO_2 .*

7 The treatment with NH_3 was effective to enhance the catalytic activity of particular metal
8 oxides such as SiO_2 for both isomerization of glucose and Knoevenagel condensation. Meanwhile,
9 TiO_2 and CeO_2 showed poor catalytic activity after the treatment with NH_3 . The catalytic activity of
10 NH_3 -treated metal oxides was presumably related to the structure of surface nitrogen species. Hence,
11 choosing SiO_2 and CeO_2 as representative samples, the structure of nitrogen was examined by
12 measuring IR spectra of the pristine and NH_3 -treated samples (Figure 3A). In a spectrum of SiO_2 , a
13 sharp absorption band for O-H stretching vibration of terminal silanol appeared at $\sim 3740\text{ cm}^{-1}$ on a
14 broad band for hydrogen-bonded silanol groups at $3500 - 3800\text{ cm}^{-1}$. For NH_3 -treated SiO_2 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 $3350 - 3450\text{ cm}^{-1}$ [37,38]. Obviously, terminal silanol reacted with
17 NH_3 to form surface NH_x groups. In contrast, such absorption bands for O-H and N-H stretching
18 vibrations were hardly observed for CeO_2 nor $\text{CeO}_2\text{-N}$. Since CeO_2 had only a small amount of
19 terminal hydroxyl groups, $\text{CeO}_2\text{-N}$ had only a limited amount of surface NH_x groups if terminal
20 hydroxyl groups reacted with NH_3 and consequently showed the poor catalytic activity.

1 The changes of functional groups on SiO₂ were clearly observed in difference IR spectra
2 (Figure 3B). After the treatment with NH₃ at 500 °C, the absorption band for terminal silanol at 3736
3 cm⁻¹ was slightly decreased, but a broad band for hydrogen-bonded silanol at 3600 – 3700 cm⁻¹ was
4 increased. Additionally, an absorption band for Si-NH₂ appeared at 3417 cm⁻¹. By the treatment at
5 600 °C, the absorption band for Si-NH₂ 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⁻¹ 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 SiO₂. Based on the above observation,
9 a plausible scheme for the formation of NH_x groups on SiO₂ is described in Scheme 3. Below 600 °C,
10 NH₃ reacted with terminal silanol to form Si-NH₂, releasing H₂O. In addition, NH₃ cleaved Si-O-Si
11 bond to form Si-NH₂ 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 SiO₂ was significantly enhanced by the treatment with NH₃ 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-NH₂ at 3417 cm⁻¹, indicating that a catalytically active
17 nitrogen site is Si-NH₂ rather than Si-NH-Si.

18 19 3.4. Difference in catalytic performance between SiO₂-N800 and MgO.

20 The catalytic performance of SiO₂-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 SiO₂-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, SiO₂-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 SiO₂-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 SiO₂-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 SiO₂-
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 SiO₂-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 CO₂-TPD
14 and the catalytic activity for the isomerization nor Knoevenagel condensation. Contrary to MgO,
15 ZrO₂, and CeO₂, which adsorbed a large amount of CO₂, NH₃-treated metal oxides including SiO₂-
16 based samples hardly adsorbed CO₂, though they showed catalytic activity for Knoevenagel
17 condensation. Additionally, while MgO promoted the reaction of fructose more than that of glucose,
18 SiO₂-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 SiO₂-N800.

1 3.5. Reaction mechanism for isomerization of saccharides over SiO₂-N800.

2 In order to demonstrate that SiO₂-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 SiO₂-N800.
4 The presence of sulfuric acid strongly inhibited the isomerization of glucose, because the
5 homogeneous acid strongly coordinated to base sites on SiO₂-N800 and inhibited reaction with
6 glucose. Furthermore, in order to demonstrate that SiO₂-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 SiO₂-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, SiO₂-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 SiO₂-N800.
12 These results surely confirmed that SiO₂-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, SiO₂-N800 as a base catalyst promoted the isomerization of glucose
2 through the proton abstraction mechanism (Scheme 4).

3

4 3.6. Reusability of SiO₂-N800.

5 In order to check the stability and reusability, the spent SiO₂-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 SiO₂-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 NH₃-treated SiO₂ was found to deserve as a promising solid base catalyst for the
15 isomerization of glucose to fructose in water. SiO₂-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-NH₂ was mainly formed by the treatment of SiO₂ with NH₃ at 500 – 600 °C and catalytic
18 activity of SiO₂ was remarkably enhanced by the treatment with NH₃. 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-NH₂ group was presumed to be a catalytically active nitrogen site on SiO₂. Unlike MgO,

subsequent reactions of fructose was not considerable over NH₃-treated SiO₂, being more suitable than MgO as a catalyst for the isomerization of glucose in terms of selectivity to fructose.

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Table 1 Surface area, nitrogen content and basicity of pristine and NH₃-treated metal oxides.

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

^a Specific surface area calculated by BET method.

^b Content of nitrogen determined by CHN analysis.

^c The number of base sites estimated by CO₂-TPD.

Table 2 Isomerization of glucose to fructose over pristine and NH₃-treated metal oxides.

Catalyst	Conversion ^a (%)	Selectivity ^b (%)	Yield ^c (%)	Saccharides recovery ^d (%)
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 ₂ O ₃	2.5	13.9	0.3	97.9
Al ₂ O ₃ -N	9.5	75.4	7.2	97.7
SiO ₂	1.5	43.4	0.6	99.2
SiO ₂ -N500	12.1	94.5	11.4	99.3
SiO ₂ -N600	21.3	94.5	20.2	98.8
SiO ₂ -N700	22.9	91.4	20.9	98.0
SiO ₂ -N800	25.0	91.3	22.8	97.8
TiO ₂	3.5	66.8	2.3	98.8
TiO ₂ -N	5.8	75.5	4.4	98.6
ZrO ₂	14.1	69.1	9.7	95.6
ZrO ₂ -N	10.8	88.9	9.6	98.8
Nb ₂ O ₅	3.5	73.4	2.6	99.1
Nb ₂ O ₅ -N	1.4	85.5	1.2	99.8
CeO ₂	5.4	4.2	0.2	94.8
CeO ₂ -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.

^a Conversion of glucose.

^{b, c} Selectivity to and yield of fructose, respectively.

^d Total amount of glucose and fructose.

Table 3 Catalytic performance of MgO and SiO₂-N800 for isomerization of saccharides.

Catalyst	Substrate	Conversion ^a	Yield ^b	Saccharide recovery ^c
		(%)	(%)	(%)
MgO	Fructose	76.3	12.3	36.0
	Glucose	34.4	25.3	91.0
SiO ₂ -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.

^a Conversion of fructose or glucose.

^b Yield of glucose or fructose.

^c Total amount of glucose and fructose.

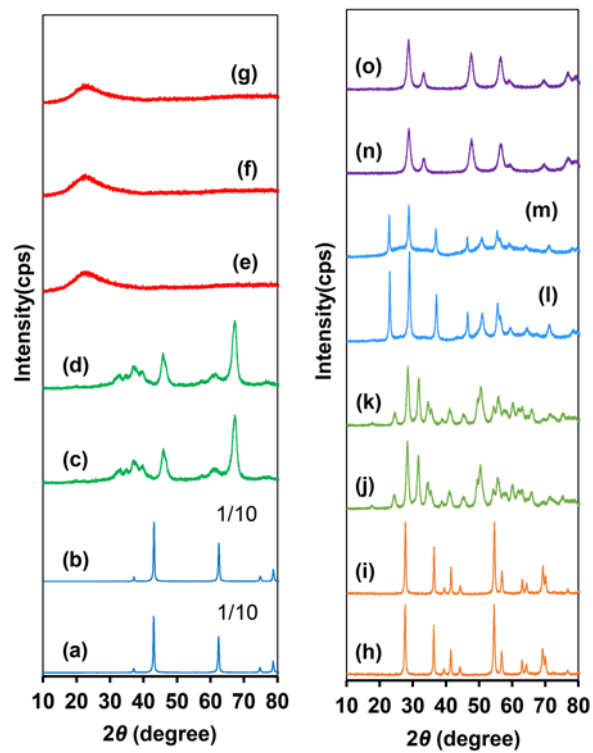


Figure 1 XRD patterns of (a) MgO, (b) MgO-N, (c) Al₂O₃, (d) Al₂O₃-N, (e) SiO₂, (f) SiO₂-N500, (g) SiO₂-N800, (h) TiO₂, (i) TiO₂-N, (j) ZrO₂, (k) ZrO₂-N, (l) Nb₂O₅, (m) Nb₂O₅-N, (n) CeO₂, and (o) CeO₂-N.

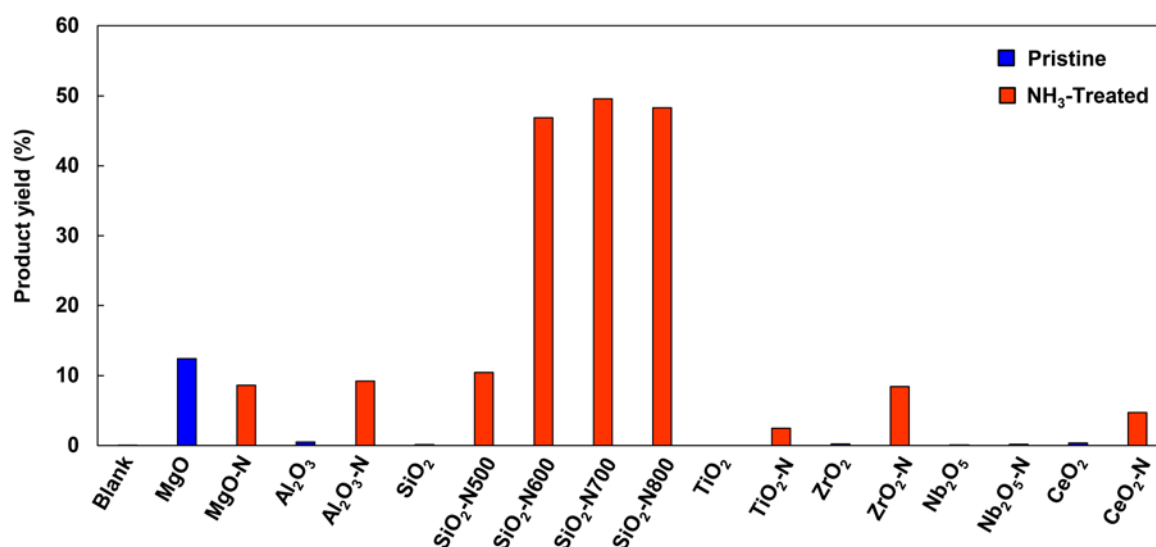


Figure 2 Catalytic performance of pristine and NH₃-treated metal oxides for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

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

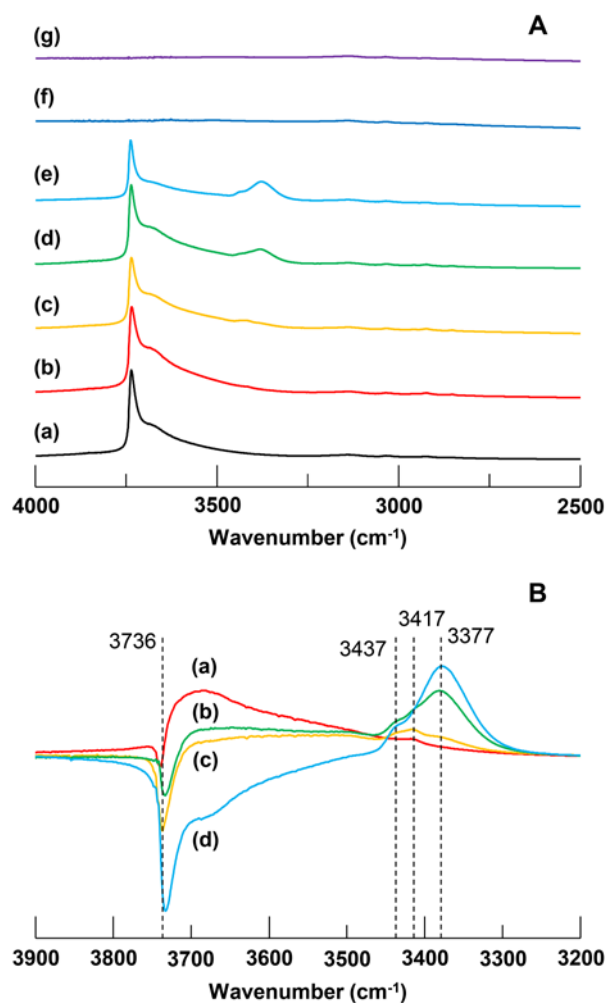


Figure 3 A: IR spectra of (a) SiO_2 , (b) $\text{SiO}_2\text{-N500}$, (c) $\text{SiO}_2\text{-N600}$, (d) $\text{SiO}_2\text{-N700}$, (e) $\text{SiO}_2\text{-N800}$, (f) CeO_2 , and (g) $\text{CeO}_2\text{-N}$. B: Difference spectra of (a) $\text{SiO}_2\text{-N500}$, (b) $\text{SiO}_2\text{-N600}$, (c) $\text{SiO}_2\text{-N700}$, and (d) $\text{SiO}_2\text{-N800}$ obtained by subtracting from the spectrum of SiO_2 .

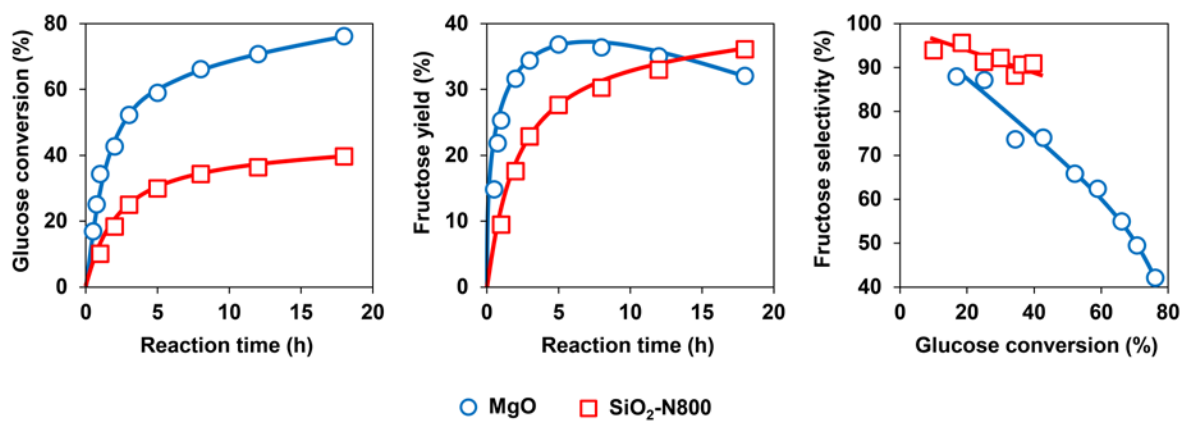


Figure 4 Isomerization of glucose to fructose over MgO and SiO₂-N800 catalysts. Reaction conditions: Catalyst, 50 mg; Glucose, 0.25 mmol; Water, 5 mL; Temperature, 80 °C.

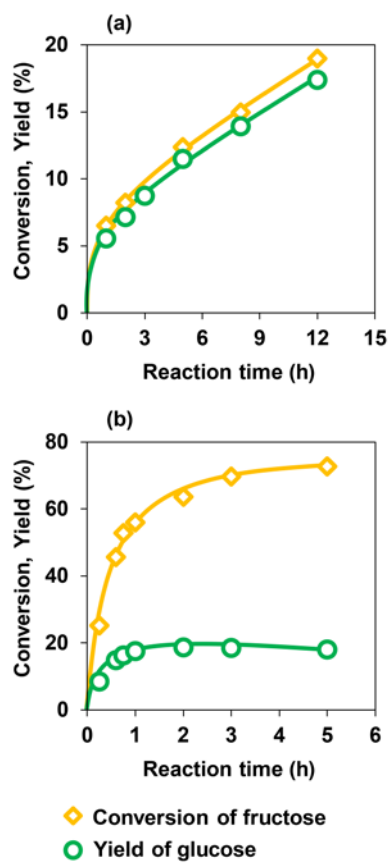


Figure 5 Isomerization of fructose to glucose over (a) SiO₂-N800 and (b) MgO catalysts. Reaction conditions: Catalyst, 25 mg; Fructose, 0.25 mmol; Water, 5 mL; Temperature, 80 °C.

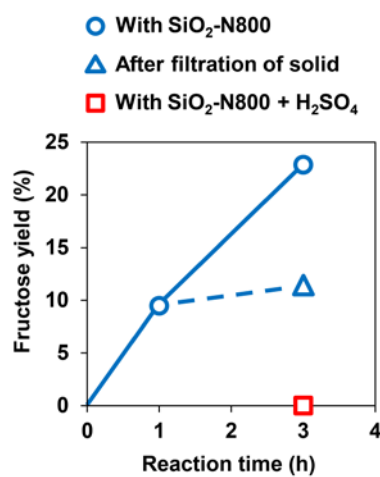
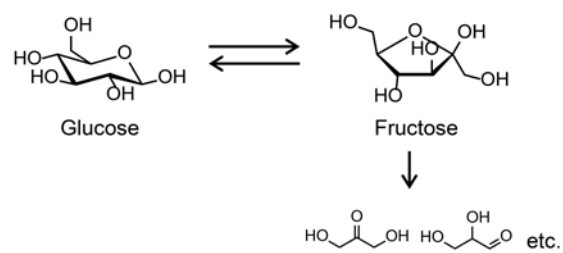
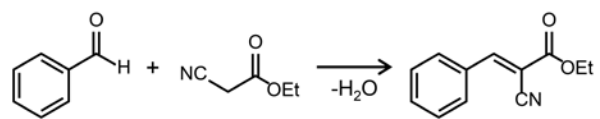


Figure 6 Influence of removal of the catalyst or addition of sulfuric acid on isomerization of glucose over SiO₂-N800.

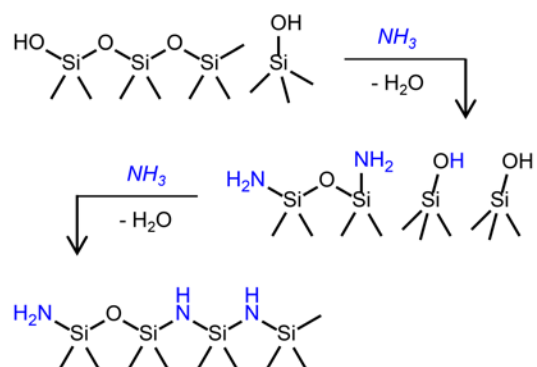
Reaction conditions: SiO₂-N800, 50 mg; Glucose, 0.25 mmol; Water, 5 mL; H₂SO₄, 0 or 0.1 mmol; Temperature, 80 °C.



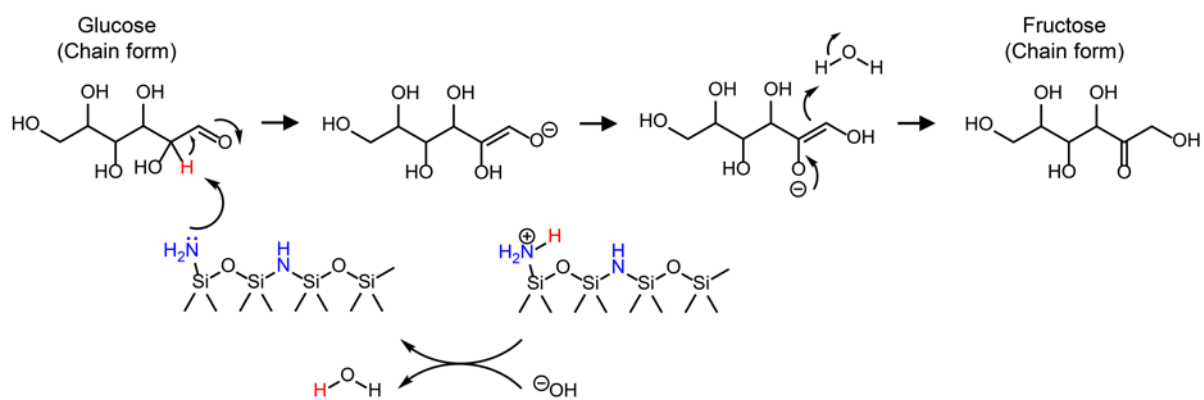
Scheme 1 Reaction pathways for isomerization of saccharides.



Scheme 2 Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.



Scheme 3 Formation of Si-NH_x groups on SiO₂.



Scheme 4 Plausible reaction mechanism for isomerization of saccharides over NH_3 -treated SiO_2 .