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Glucose Isomerization Using Alkaline and Alkaline Earth Titanates

Junya Ohyama,*[a, b] Yutong Zhang,[a] Jun Ito,[a] Atsushi Satsuma*[a, b]

Abstract: Glucose isomerization was performed using various titanate catalysts, including $SrTiO_3$, $BaTiO_3$, $CaTiO_3$, $Na_2Ti_6O_{13}$, $K_2Ti_6O_{13}$, and $Sr_3Ti_2O_7$, prepared using a conventional solid phase method. Among the titanates, $SrTiO_3$, $CaTiO_3$, and $Na_2Ti_6O_{13}$ offered a relatively high fructose yield (32%) with high selectivity (68–78%). The yields are comparable to previously reported yields using a tin-modified BEA zeolite, which shows high efficiency for glucose isomerization as a Lewis acid catalyst. A study of the mechanism of glucose isomerization on a $SrTiO_3$ catalyst surface using ^{1}H-NMR spectroscopy suggested that the titanates catalyze the isomerization as base catalysts. Thus, the effects of basicity of the titanates on glucose isomerization were investigated in terms of base quantities and strength of the titanates. The analysis was performed by an acid-base titration method and FT-IR spectroscopy using $CHCl_3$ as a probe molecule. It is proposed that glucose isomerization on the titanates is dependent not only on the base amounts, but also on the base strength.

Introduction

Glucose isomerization has generated renewed interest because it is an intermediate step in biorefinery processes that convert cellulose to fuels and chemicals.[1-5] Currently, glucose/xylose isomerase is used for the isomerization of glucose to fructose in the food industry (42% fructose yield at 60 °C), e.g., production of high fructose syrup.[1, 6] However, the enzymatic process is expensive due to the strict control of reaction conditions. Thus, highly active, robust, and cheap inorganic catalysts are required.[1] A homogeneous base such as sodium hydrate is known to catalyze the isomerization of glucose, but often offers a low yield of fructose (< 10%) due to degradation of monosaccharides into byproducts.[1, 7-8] Compared to a homogeneous base, relatively higher yields of fructose can be obtained using a heterogeneous base.[9-11] For example, it has been reported that hydrotalcite offers fructose in 25% yield.[9] Metallosilicates as base catalysts also offer high fructose yields (20–40% yield of fructose).[10-11] Interestingly, the catalytic performance of hydrotalcite and metallosilicate in the isomerization reaction was improved through control of their basicity.[9, 11] Heterogeneous Lewis acids also catalyze the isomerization.[1, 7, 12-14] Among acid-base catalysts for glucose isomerization reported so far, a tin-modified BEA zeolite, which functions as a Lewis acid catalyst, exhibits high efficiency for the isomerization reaction in aqueous media (32% fructose yield).[1]

Alkaline and alkaline earth metal titanates as catalyst materials have been extensively studied, particularly due to their high photocatalytic activity for water splitting, CO_2 reduction, CH_4 reforming, etc.[15-19] They are also utilized as supports of metal catalysts in the oxidation of hydrocarbons.[20-21] It is expected that the acid-base properties of the titanates would contribute to their unique catalytic activity through adsorption of reactants and products. However, there are only a few reports on their acid-base property. Acidity of $SrTiO_3$ and $BaTiO_3$, which have a perovskite structure, has been investigated using chemisorption of pyridine and CO_2 adsorption, followed by Raman and infrared (IR) spectroscopy, and CO_2 temperature programed desorption (TPD).[21-23] The data indicated that the perovskite type titanates have basicity and weak Lewis acidity. In addition, acid-base properties of the perovskite type titanates can be controlled by the counter cations.[24] The controllable acid-base property is expected to be useful towards tailoring finely tuned acid-base catalysts. However, to our knowledge, titanates have been rarely applied to acid-base reactions.[24] On the other hand, various metallates have been developed as acid-base catalysts. One of the most extensively studied metallates is heteropoly compounds.[25-27] Variation of counter cations for heteropoly acid tunes the acidity, and promotes efficient catalytic reactions. For example, one of the authors of this paper reported that the variation of counter cations for a heteropoly acid enhanced hydrolysis of cellulose and Friedel–Crafts acylation and alkylation.[28-29]

Herein, we applied various alkaline and alkaline earth titanates as acid-base catalysts in glucose isomerization. The acid-base properties of titanates, used as catalysts for glucose isomerization, were analyzed using proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, acid-base titration, and Fourier transform infrared (FT-IR) spectroscopy.

Results and Discussion

Figure 1 shows the XRD patterns of the prepared titanates. The XRD data confirms that $SrTiO_3$, $BaTiO_3$, and $CaTiO_3$ have perovskite structures (PDF2 nos. 01-080-1935, 01-079-2264, and 01-070-8503), and $Na_2Ti_6O_{13}$, $K_2Ti_6O_{13}$, and $Sr_3Ti_2O_7$ have perovskite-like structures (PDF2 nos. 01-073-1398, 01-074-0275, and 01-076-0740). The specific surface areas of the titanates determined by N_2 adsorption were 1.8-5.6 m^2 g^{-1}. The structures and surface areas of the samples are listed in Table 1.

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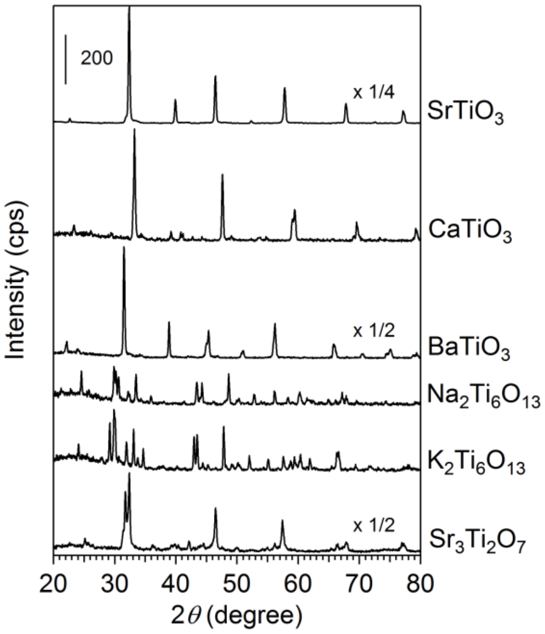

Figure 1. XRD of the titanates prepared in this study.

The results of glucose isomerization using the alkaline and alkaline earth titanates are presented in Table 1. Fructose and mannose were obtained as products of the isomerization reaction. The other products are likely sugar derived acids.[8] A comparison between the various titanates shows that SrTiO$_3$, CaTiO$_3$, and Na$_2$Ti$_6$O$_{13}$ offer relatively high yields of fructose (32%). Among the three titanates, SrTiO$_3$ showed the highest selectivity for fructose (78%). The fructose yield and selectivity for SrTiO$_3$ is superior to that of TiO$_2$ and SrCO$_3$, which are the precursors of SrTiO$_3$ (Table 1, entries 7 and 8). Thus, the titanate structure improves the performance of glucose isomerization. The reaction performance of SrTiO$_3$ was also better than La$_2$O$_3$ and hydrotalcite, which are conventional base catalysts (Table 1, entries 9 and 10). In addition, the fructose yield and selectivity using SrTiO$_3$ was comparable to that of a tin-modified BEA zeolite, a Lewis acid catalyst used in a previous report (32% fructose yield with 71% selectivity by 45% glucose conversion).[1]

To examine the heterogeneous catalysis of SrTiO$_3$, a leaching test was performed. Figure 2 shows the time course of glucose conversion using SrTiO$_3$, with and without the removal of SrTiO$_3$ in the middle of the reaction. As presented in Figure 2(a), an increase in glucose conversion stopped at 15 min when SrTiO$_3$ was removed by centrifugation, although glucose conversion continued to increase for 30 min without the removal SrTiO$_3$. This indicates that SrTiO$_3$ catalyzes the glucose isomerization as a heterogeneous catalyst. The reaction solution using SrTiO$_3$ was analyzed using ICP and 0.033 mmol of Sr was detected in the reaction solution. The leaching of Sr was much less than the total amount of Sr in SrTiO$_3$ used as catalyst (ca. 3%). Sugar derived acids as byproducts might be responsible for the leaching.[8] Based on the above results, it is reasonable to assume that the titanates function as heterogeneous catalysts for the glucose isomerization, but their alkaline or alkaline earth metal components partly (probably from surfaces of the titanates) leach out from the reaction solution.

Table 1. Results of glucose isomerization, specific surface areas, and base amounts of catalysts.

Entry	Catalyst	Results of glucose isomerization[a] (%)				S$_{BET}$[b] (m$_2$ g^{-1})	Base amount[c] (mmol g^{-1})
		Glucose cov.	Fructose yield	Mannose yield	Fructose selc.		
1	SrTiO$_3$	41	32	5	78	5.3	0.15
2	BaTiO$_3$	33	23	3	70	4.8	0
3	CaTiO$_3$	47	32	8	68	3.4	0.075
4	Na$_2$Ti$_6$O$_{13}$	45	32	7	71	1.8	0.175
5	K$_2$Ti$_6$O$_{13}$	23	17	-	74	5.6	0.025
6	Sr$_3$Ti$_2$O$_7$	60	34	10	57	5.0	1.2
7	TiO$_2$	8	6	-	75	79.5	-
8	SrCO$_3$	17	8	-	47	-	-
9	Hydrotalcite	77	20	10	26	18.1	-
10	La$_2$O$_3$	41	18	17	44	7.0	-
11	Recycled	32	25	4	78	-	-

[a] Reaction conditions: 2 mL of 10wt% glucose aq.; 0.2 g of catalyst; 110 °C, 1 h. [b] Specific surface areas were determined using the BET method. [c] Determined using an acid-base titration method using phenolphthalein as an indicator.

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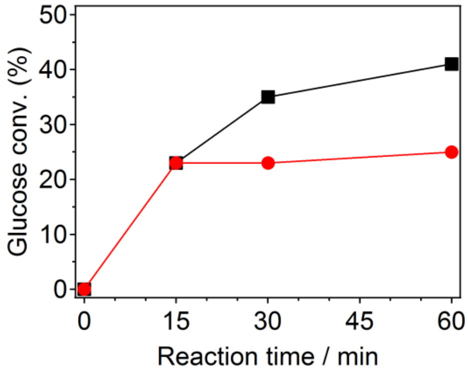
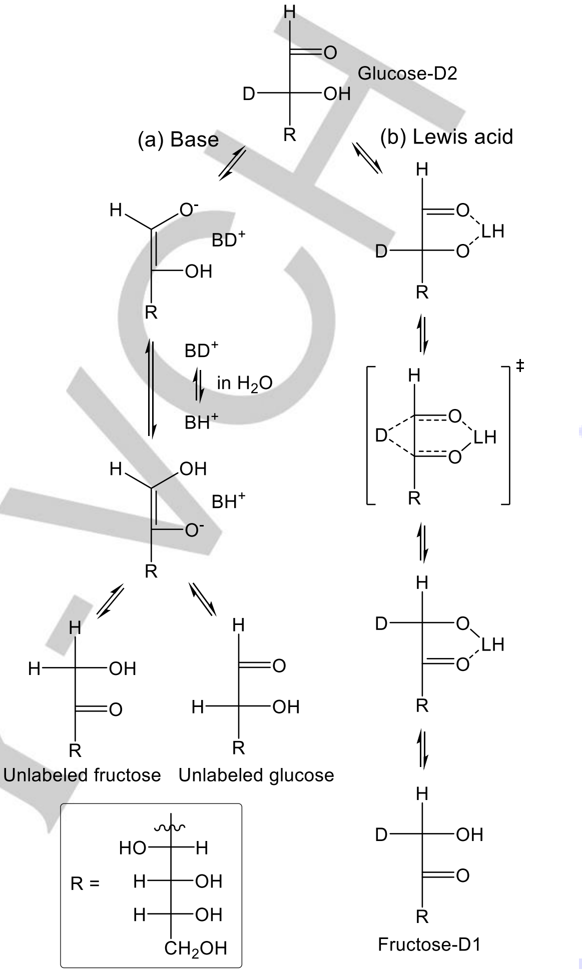


Figure 2. The time course of glucose conversion using $SrTiO_3$: (a) removal of $SrTiO_3$ at 15 min (red circle); (b) without the removal (black square).

To evaluate the reusability of the catalyst, $SrTiO_3$ was recycled by filtration after 1 h of the first reaction, and then dried at 80 °C. The recycled $SrTiO_3$ exhibited lower glucose conversion and fructose yield compared to the fresh $SrTiO_3$ (c.f. Table 1, entries 1 and 11). Thus, $SrTiO_3$ does not have high reusability, which might be related to the leaching of Sr from $SrTiO_3$ surface. Suppression of the leaching and improvement in reusability are challenges to be addressed in the future.

Davis et al.[7] evaluated the mechanism of glucose isomerization using NMR analyses of reaction solutions of deuterated glucose at C-2 position. The glucose isomerization is catalyzed by a base and a Lewis acid, which follow different reaction mechanism as presented in Scheme 1.[7] When using Lewis acid catalysts, the glucose isomerization proceeds via intramolecular hydride shifts from C-2 position to C-1 position as glucose-D2 is transformed to fructose-D1. On the other hand, when using base catalysts, such as NaOH, proton transfer from glucose C-2 position to base catalysts causes the isomerization. In the case of glucose-D2 isomerization in H_2O, the deuteron-abstracted glucose-D2 abstracts a proton from H_2O solvent, since H_2O is a larger proton source than deuterons generated from glucose-D2. It should be also noted that the reverse isomerization of fructose to glucose via the proton transfer mechanism yields non-D-labeled glucose from glucose-D2. Figure 3 shows a NMR spectrum of glucose-D2, reacted with $SrTiO_3$ in H_2O, along with spectra of glucose-D2 reacted in NaOH aq., glucose-D2, and unlabeled glucose as references. The reacted glucose-D2 with $SrTiO_3$ showed resonances arising from a proton in the C-2 position of unlabeled glucose at δ = 3.25 ppm (Figure 3(a)), which also appear in the spectrum of glucose-D2 reacted in 2.5 mM NaOH aq. (Figure 3(b)). This indicates that $SrTiO_3$ functions as a base catalyst in the isomerization reaction.



Scheme 1. Mechanism of glucose isomerization catalyzed by (a) base and (b) Lewis acid (B: Base, L: Lewis acid).[7]

Based on the above NMR analyses, basicity of the alkaline and alkaline earth titanates is assumed to affect the efficiency of glucose isomerization. Thus, we investigated the effect of basicity of the titanates on the glucose isomerization reaction. Base amounts of the titanates were evaluated using a titration method with phenolphthalein as an indicator. In Figure 4, the glucose conversion and the fructose yields on the titanates (Table 1, entries 1–6) are plotted against their base amounts. Both glucose conversion and fructose yield tend to increase with the base amount. Effect of base amounts on fructose selectivity was also investigated. The fructose selectivity was evaluated at 40–50% glucose conversion by modifying catalyst amounts and/or reaction time in the case of the reaction using $BaTiO_3$ and $Sr_3Ti_2O_7$. Figure 5 presents the fructose selectivity as a function of the base amount used for the reaction. The fructose selectivity increases with the base amount from 0.075 to 0.175 mmol, and then decreases slightly. The effect of the base amounts on glucose isomerization is similar to the effect of pH reported by Tessonnier et al.[8] using various amounts of trimethylamine (TEA) as a base catalyst. Based on their study, the reason for the dependence seen in Figures 4 and 5 can be attributed to the fact that base amounts strongly affect reaction rates of both glucose isomerization and degradation of acyclic forms of glucose and fructose.

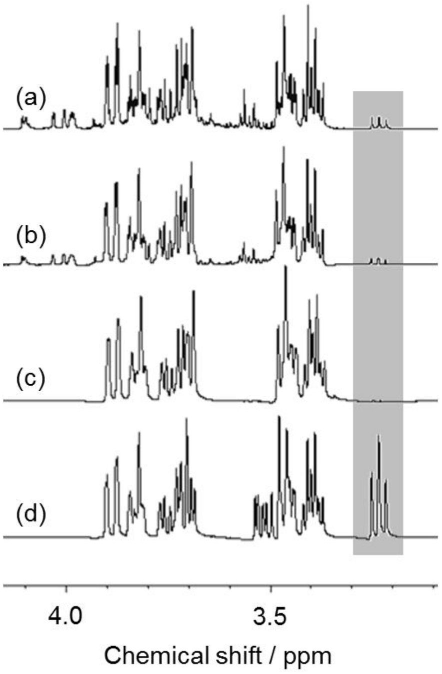


Figure 3. (a) NMR spectrum of glucose-D2 reacted with $SrTiO_3$ in H_2O, along with spectra of (b) glucose-D2 reacted in 2.5 mM NaOH aq., (c) glucose-D2, and (d) unlabeled glucose as references.

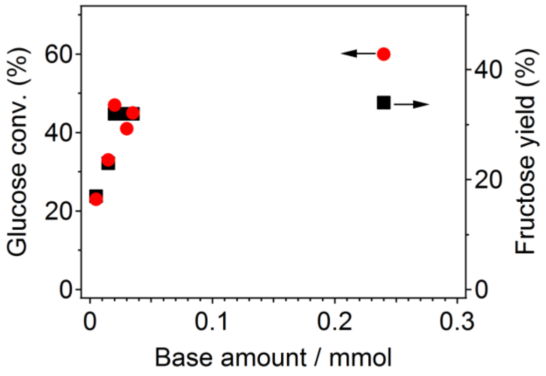


Figure 4. Glucose conversion (red circle) and the fructose yields (black square) on the titanates (Table 1, entries 1–6) plotted against base amounts used for reaction (catalyst amount: 0.2 g).

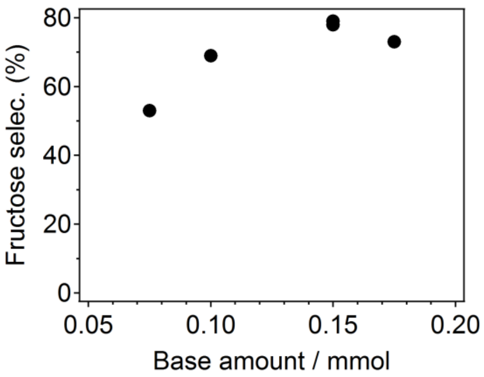


Figure 5. Fructose selectivity (at 40–50% glucose conversion) plotted against base amounts used in the reaction. In the case of the reactions using $BaTiO_3$ and $Sr_3Ti_2O_7$, the reaction time or catalyst amount was modified: 2 h for $BaTiO_3$; 0.025 g of catalyst for $Sr_3Ti_2O_7$. The figure does not report data using $K_2Ti_6O_{13}$, because $K_2Ti_6O_{13}$ (0.2 g) did not afford 40–50% glucose conversion at 110 °C for 6 h. The other data are from Table 1, entries 1, 3, and 4.

Table 2 shows the results of glucose isomerization using 0.4 g of $BaTiO_3$ and 0.025 g of $Sr_3Ti_2O_7$, which have the same base amount as 0.2 g of $SrTiO_3$. The reaction using 0.4 g of $BaTiO_3$ resulted in lower glucose conversion and fructose yield and selectivity compared to 0.2 g of $SrTiO_3$ (Table 1, entry 1) and 0.025 g of $Sr_3Ti_2O_7$ (Table 2). The result implies that other base properties could contribute to the reactivity. Therefore, we investigated base strength of the titanates by FT-IR spectroscopy using $CHCl_3$ adsorption.[30-31] Figure 6 shows the IR bands due to C-H stretching mode of adsorbed $CHCl_3$ on the various titanates. The wavenumber of the band of C-H stretching varied with the titanates, indicating that the titanates have different base strength. Since the band shift to lower wavenumber indicates stronger base, the base strength of the titanates is in the order $BaTiO_3 < SrTiO_3 < K_2Ti_6O_{13} < Na_2Ti_6O_{13} < CaTiO_3 < Sr_3Ti_2O_7$. Accordingly, $BaTiO_3$ is the weakest base among the titanates used in this study. The weak basicity of $BaTiO_3$ is a possible reason for the low catalytic activity of $BaTiO_3$. Conversely, a stronger base than $BaTiO_3$ (e.g., $SrTiO_3$ and $Sr_3Ti_2O_7$) is considered to be effective for the isomerization reaction. Therefore, we propose that base strength of solid base catalysts also contribute to glucose isomerization performance in

Table 2. Results of glucose isomerization using $BaTiO_3$ and $Sr_3Ti_2O_7$ with the same amount of 0.2 g of $SrTiO_3$ (Table 1, entry 1).

Catalyst	Results of glucose isomerization[a] (%)				Base amount[b] (mmol)
	Glucose cov.	Fructose yield	Mannose yield	Fructose selc.	
$BaTiO_3$ 0.4 g	35	0.15	5	78	0.03
$Sr_3Ti_2O_7$ 0.025 g	33	0	3	70	0.03

[a] Table Footnote. [b] …

addition to base amount.

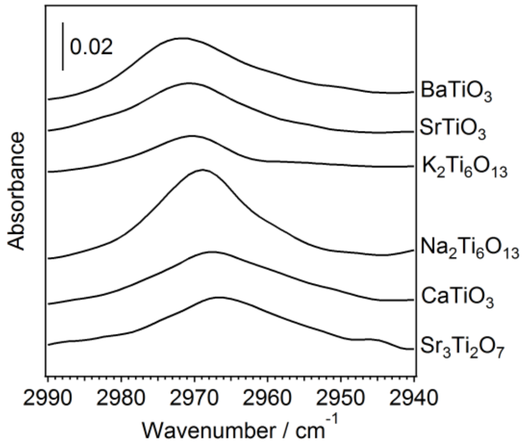


Figure 6. FT-IR spectra of $CHCl_3$ adsorbed on the titanates.

Conclusions

The various titanates, including $SrTiO_3$, $BaTiO_3$, $CaTiO_3$, $Na_2Ti_6O_{13}$, $K_2Ti_6O_{13}$, and $Sr_3Ti_2O_7$, catalyzed glucose isomerization. In particular, $SrTiO_3$, $CaTiO_3$, and $Na_2Ti_6O_{13}$ offered a high fructose yield and selectivity under the reaction conditions employed in this study (10 wt% glucose aq., 0.2 g of catalyst, 110 °C, 1 h). The ^{1}H NMR analysis of glucose-D2 after reaction on $SrTiO_3$ suggested that the base sites on the titanates are effective for the isomerization. The analysis of base properties of the titanates using an acid-base titration method and $CHCl_3$ adsorption FT-IR spectroscopy indicated that the various titanates have different base amounts and strength. Based on the dependence of the glucose isomerization on the base properties, we propose that both base amount and strength of solid base catalysts (e.g., the titanates) contribute to the efficiency of the glucose isomerization process. The results would be useful towards developing solid base catalysts for glucose isomerization.

Experimental Section

Catalyst preparation. Alkaline and alkaline earth titanates, $SrTiO_3$, $BaTiO_3$, $CaTiO_3$, $Na_2Ti_6O_{13}$, $K_2Ti_6O_{13}$, and $Sr_3Ti_2O_7$ were prepared by a solid state reaction. The respective alkaline carbonates (Kishida Chemical Co., Ltd.) and TiO_2 (JRC-TIO-8 procured from Catalysis Society of Japan, anatase phase) as precursors were homogeneously mixed using a ball mill in the composition ratio of each titanate, and calcined at 1000 °C under air for 10 h. The resulting powders were washed with hot water, and dried at 80 °C.

Evaluation of catalytic activity. Glucose isomerization was performed at 110 °C using 2 mL of 10 wt% aqueous glucose solution containing 0.2 g of catalyst unless otherwise stated. In addition to the titanate catalysts, TiO_2 (JRC-TIO-8), $SrCO_3$ (Kishida Chemical Co., Ltd.), La_2O_3 (Kishida Chemical Co., Ltd.), hydrotalcite (Kyowa Chemical Industry Co. Ltd.) were used as catalysts for comparison. The catalysts were pre-treated at 500 °C under 100 mL min^{-1} of O_2 flow for 30 min just before use for the glucose isomerization reaction. The solutions from the reaction were analyzed by means of high performance liquid chromatography (HPLC) using a JASCO LC-2000 Plus series HPLC equipped with a Shim-pack SPR-Ca (250 × 7.8 mm) column. For investigating the reaction mechanism on $SrTiO_3$, deuterated glucose at C-2 position (glucose-D2) was used as a reactant. The reaction of glucose-D2 was performed using 2 mL of 1 wt% glucose-D2 aqueous solution with 0.2 g of $SrTiO_3$ at 90 °C for 1h. After reaction, H_2O solvent was evaporated, and the residue was dissolved in D_2O to acquire a NMR spectrum.

Characterization. X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex II/AP diffractometer with Cu $K\alpha$ radiation. The specific surface area of the samples was determined from N_2 adsorption using Brunauer–Emmett–Teller (BET) method (BELSORP-28, BEL Japan). The leaching of alkaline and alkaline earth metals in reaction solutions were analyzed using a sequential inductively coupled plasma (ICP) spectrometer (Thermo Jarrel Ash IRIS/AP). ^{1}H-NMR spectra were measured in D_2O on a Bruker 500 MHz NMR spectrometer. Base amounts of the titanates were evaluated using an acid-base titration method using phenolphthalein as an indicator. Prior to a titration, the titanates (0.025–0.1 g) were pre-treated in a test tube at 500 °C under O_2 flow for 30 min. After cooling to room temperature, 2 mL of water/ethanol mixture (1/4 v/v), and then a few drops of 50 mM phenolphthalein solution in ethanol were added to the tube. 50 mM benzoic acid solution in ethanol was dropped into the suspension with stirring until the color of phenolphthalein faded. The base amounts of the titanates were evaluated from the amount of benzoic acid solution added. FT-IR spectra of adsorbed $CHCl_3$ were recorded on a JASCO FT/IR-6100 (JASCO Co.) equipped with a MCT detector with a resolution of 4 cm^{-1}. Samples were pressed into wafers of 20 mm diameter. The wafers were pre-treated under 10% O_2 flow (Ar balance, 100 mL min^{-1}) at 500 °C for 10 min. After cooling to 150 °C, background spectra were acquired. The wafers were then exposed to $CHCl_3$ vapor (2 μL in liquid) under Ar flow (90 mL min^{-1}) for 10 min, and IR spectra of adsorbed $CHCl_3$ were recorded.

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Keywords: glucose isomerization • titanate • base catalyst

[1] M. Moliner, Y. Román-Leshkov, M. E. Davis, *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 6164.
[2] K. Nakajima, Y. Baba, R. Noma, M. Kitano, J. N. Kondo, S. Hayashi, M. Hara, *J. Am. Chem. Soc.* **2011**, *133*, 4224.
[3] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411.
[4] G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* **2005**, *308*, 1446.
[5] R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499.
[6] Y. Tewari, *Appl. Biochem. Biotechnol.* **1990**, *23*, 187.
[7] Y. Román-Leshkov, M. Moliner, J. A. Labinger, M. E. Davis, *Angew. Chem. Int. Ed.* **2010**, *49*, 8954.
[8] J. M. Carraher, C. N. Fleitman, J.-P. Tessonnier, *ACS Catal.* **2015**, *5*, 3162.

[9] C. Moreau, R. Durand, A. Roux, D. Tichit, *Appl. Catal. A* **2000**, *193*, 257.

[10] R. O. L. Souza, D. P. Fabiano, C. Feche, F. Rataboul, D. Cardoso, N. Essayem, *Catal. Today* **2012**, *195*, 114.

[11] S. Lima, A. S. Dias, Z. Lin, P. Brandao, P. Ferreira, M. Pillinger, J. Rocha, V. Calvino-Casilda, A. A. Valente, *Appl. Catal. A* **2008**, *339*, 21.

[12] Y. Román-Leshkov, M. E. Davis, *ACS Catal.* **2011**, *1*, 1566.

[13] R. Bermejo-Deval, R. Gounder, M. E. Davis, *ACS Catal.* **2012**, *2*, 2705.

[14] R. Bermejo-Deval, R. S. Assary, E. Nikolla, M. Moliner, Y. Román-Leshkov, S.-J. Hwang, A. Palsdottir, D. Silverman, R. F. Lobo, L. A. Curtiss, M. E. Davis, *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 9727.

[15] K. Shimura, H. Kawai, T. Yoshida, H. Yoshida, *ACS Catal.* **2012**, *2*, 2126.

[16] K. Shimura, H. Kawai, T. Yoshida, H. Yoshida, *Chem. Commun.* **2011**, *47*, 8958.

[17] K. Shimura, H. Yoshida, *Energy Environ. Sci.* **2010**, *3*, 615.

[18] H. Yoshida, L. Zhang, M. Sato, T. Morikawa, T. Kajino, T. Sekito, S. Matsumoto, H. Hirata, *Catal. Today* **2015**, *251*, 132.

[19] T. K. Townsend, N. D. Browning, F. E. Osterloh, *ACS Nano* **2012**, *6*, 7420.

[20] M. Daturi, G. Busca, G. Groppi, P. Forzatti, *Appl. Catal. B* **1997**, *12*, 325.

[21] M. Daturi, G. Busca, R. J. Willey, *Chem. Mater.* **1995**, *7*, 2115.

[22] G. Busca, V. Buscaglia, M. Leoni, P. Nanni, *Chem. Mater.* **1994**, *6*, 955.

[23] J. M. G. Amores, V. S. Escribano, M. Daturi, G. Busca, *J. Mater. Chem.* **1996**, *6*, 879.

[24] W. Ding, Y. Chen, X. Fu, *Appl.Catal. A* **1993**, *104*, 61.

[25] N. Mizuno, M. Misono, *Chem. Rev.* **1998**, *98*, 199.

[26] T. Okuhara, N. Mizuno, M. Misono, in *Advances in Catalysis, Vol. 41* (Eds.: W. O. H. D.D. Eley, G. Bruce), Academic Press, **1996**, pp. 113.

[27] I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171.

[28] K.-i. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya, A. Satsuma, *Green Chem.* **2009**, *11*, 1627.

[29] K.-i. Shimizu, A. Satsuma, *Energy Environ. Sci.* **2011**, *4*, 3140.

[30] M. Tamura, K.-i. Shimizu, A. Satsuma, *Appl. Catal. A* **2012**, *433・434*, 135.

[31] T. Komanoya, K. Nakajima, M. Kitano, M. Hara, *J. Phys. Chem. C* **2015**, *119*, 26540.

Entry for the Table of Contents

Layout 1:

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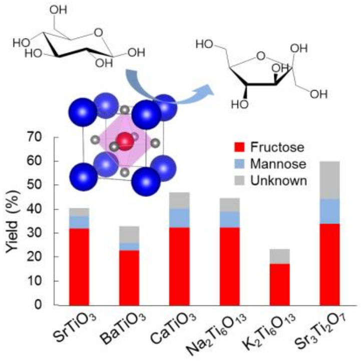
Glucose isomerization was carried out using various titanate catalysts, including $SrTiO_3$, $BaTiO_3$, $CaTiO_3$, $Na_2Ti_6O_{13}$, $K_2Ti_6O_{13}$, and $Sr_3Ti_2O_7$ prepared using a conventional solid phase method. Among the titanates, $SrTiO_3$, $CaTiO_3$, and $Na_2Ti_6O_{13}$ offered relatively high fructose yield (32%) with high selectivity (68–78%). Glucose isomerization on the titanates was dependent on both base amount and strength.



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