Isomerization of glucose at hydrothermal condition with TiO$_2$, ZrO$_2$, CaO-doped ZrO$_2$ or TiO$_2$-doped ZrO$_2$

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A R T I C L E   I N F O

A B S T R A C T

Catalytic activity of TiO$_2$, ZrO$_2$ and ZrO$_2$ solid solutions (with CaO or TiO$_2$) for the isomerization of glucose into fructose under hydrothermal conditions (120–180 °C for 5–15 min reaction time) was evaluated by experimental kinetic studies and surface acidity–basicity measurements. Kinetic studies were conducted with batch reactors heated by microwave. Under hydrothermal conditions regardless of the temperature, fructose yield was always below 10% and fructose selectivity was rapidly decreased with increasing glucose conversion. By adding 10 mM NaOH, fructose yield reached 20% at 160 °C for 5 min. In the presence of TiO$_2$, fructose yield and selectivity were similar (160 °C, 47% of glucose conversion and 14% fructose yield). ZrO$_2$ showed higher catalytic activity (160 °C, 63% glucose conversion and 21% fructose yield) compared with TiO$_2$. The catalytic activity of TiO$_2$ doped ZrO$_2$ was between TiO$_2$ and ZrO$_2$. To increase the basicity of ZrO$_2$, CaO was doped into the ZrO$_2$ matrix. For experiments with the 24 wt% CaO doped ZrO$_2$, fructose selectivity was higher than 70% even at 30% glucose conversion at 160 °C for 15 min. For systematical understanding catalytic activity of the metal oxides used, acidity and basicity of the catalysts were measured by temperature programmed desorption (TPD) using either CO$_2$ or NH$_3$. It was found that basicity on the surface increased with increasing the amount of CaO in the ZrO$_2$ solid solution while acidity increased with amounts of TiO$_2$. For a simple network model of glucose reactions, rate constants were fitted to the data assuming a simple network model and they were completed with the acid-base properties of TiO$_2$, ZrO$_2$ and CaO doped and TiO$_2$ doped ZrO$_2$. As a result, the reactivity was found to be correlated with the ratio of the base to acid sites on the surface and fructose formation was linearly proportional to the base/acid mole ratio on the surface of the catalysts.

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1. Introduction

Glucose is widely found in natural resources such as carbohydrates, saccharides and cellulosic materials and it is an important chemical for food and biomass chemistry. Transformation of glucose into its isomer, namely fructose, is important as a primary step for modifying of sugars for dietary purposes or for as chemical use.

It is well known that the isomerization of glucose into fructose is catalyzed by alkali (or solid base) catalysts through proton transfer or Lewis acid catalysts through hydride transfer. Liu et al. [1] found high catalytic activity of organic amines on glucose isomerization in hot water at 100 °C for 30 min reaction time, where glucose conversion was 51% and fructose yield was 32% (fructose selectivity:

63%). However, homogeneous catalysts have disadvantages in their reuse and recycle due to the difficulty of their separation from the reaction products. To overcome the difficulty of reuse and recycle homogenous catalysts, solid catalysts are preferable.

Tin coated zeolite, which is a solid Lewis acid catalyst, has been demonstrated to have high catalytic activity for glucose isomerization in water at 110–140 °C, giving around 30% of fructose yield at 50% of glucose conversion [2]. Tin-coated zeolite, on the other hand, requires a complicated and long-period production process (hydrothermal treatment at 180 °C for up to 40 d). Alkali-metal ion exchange zeolite has also been demonstrated to have activity for glucose isomerization [3–5] but metal cations tend to leach from the surface of the zeolites under hydrothermal conditions (90–95 °C). Talcites have been tested for glucose isomerization in hot water [3,5,6] and leaching of magnesium ion in the talcite was observed [6].

As a water-tolerate solid base catalyst, metallosilicates [7], zirconia promoted with Cs [8], zironosilicate [9] and zirconium carbonate [10] have been tested to isomerize glucose into fructose under hydrothermal conditions at 80–150 °C. Zirconiumsilicate and zirconium carbonate have good stability under hydrothermal conditions and their catalytic activity is also high (for zirconiumsilicate, glucose conversion was 46% and fructose selectivity was 52% at 80 °C for 1 h; for ziroconium carbonate, glucose conversion was 45% and fructose selectivity was 76% at 120 °C for 20 min). Surface basicity of these ziroconium-based catalysts was evaluated by CO_2-TPD [9] or titration method [10] and these basic properties were considered to be related to the catalytic activity, but the correlation between surface properties and catalytic activity was not clarified. Previously, anatase-TiO_2 and tetragonal ZrO_2, which are stable under hydrothermal conditions at 200 °C, were used to study the of isomerization glucose [11,12] and it was found that zirconium could promote the reaction. Surface basicity and acidity of the zirconium was evaluated by CO_2- and NH_3-TPD and it was considered that higher basicity of the zirconia was closely related to its higher catalytic activity than anatase-TiO_2, of which its basicity was weaker [12]. For the design of an appropriate solid base catalyst for glucose isomerization having water-tolerance, zirconium-based catalyst seems to be preferable.

According to Moreau et al. [5], the rate of glucose isomerization depends on pH (NaOH amount) of water media in hot water (90 °C). Lee et al. [13] clearly showed that the acidity–basicity of zirconium can be controlled by doped-metal cation and their amount. In this work, catalytic activity of CaO- or TiO_2-solid solutions with zirconium for glucose isomerization in hydrothermal water at 120–180 °C was evaluated with experimental reaction studies and correlation of the rates with the catalyst surface acidity–basicity. For comparison, anatase-TiO_2 and tetragonal-ZrO_2 were tested as catalysts for glucose isomerization along with glucose reaction with and without NaOH. To determine the acidity–basicity of the metal oxides used in this study, temperature programmed desorption method (TPD: NH_3-TPD for acidity and CO_2-TPD for basicity) was used. Based on the kinetic data, a simple network kinetic model was developed and the rate constant of each reaction step was determined by fitting a model to the experimental data. The correlation between the rate constant and acidity-basicity of the metal oxides was elucidated.

2. Experimental

2.1. Materials

Anatase TiO_2 was purchased from Wako Co., Ltd., and used as it is. Tetragonal ZrO_2 was prepared from $Zr(OH)_4$ obtained from Nakarai Tesque (Kyoto, Japan) by calcination at 400 °C. The crystal structure of the calcined ZrO_2 was found to be mixture of monoclinic and tetragonal from determination by XRD analysis [12]. ZrO_2 solid solutions (CaO or TiO_2 were doped into the ZrO_2 matrix) was provided by Daiichi Kigenso Co., Ltd. (Osaka, Japan). The doped amounts of CaO were 4.3, 14, and 24 mol% denoted as Ca-4.3, Ca-14, and Ca-24, respectively and those of TiO_2 were 7.5 and 15 mol% denoted as Ti-7.5 and Ti-15, respectively. These CaO- and TiO_2-doped ZrO_2 were calcined at 700 °C for 1 h. The structure of all the doped ZrO_2 was cubic (from XRD analysis, not shown here) regardless of the kind and amount of doped metal oxide. Table 1 shows some physical properties of the metal oxides that are used in this study. The amounts of acid and base sites were measured by a temperature programmed desorption (TPD) method. Probe substrate for acid and base sites were NH_3 and CO_2 respectively. The procedures and the conditions of TPD measurement were described below. In summary, ZrO_2 has the similar amount of acid and base

sites. The amount of base sites on CaO-doped ZrO_2 was higher than that of acid sites and the basicity increased with increasing the doped amount of CaO. On the TiO_2-doped ZrO_2 and the anatase-TiO_2, the amount of acid sites was higher than that of base sites.

Glucose and fructose were purchased from Wako-Pure Chemicals, Co., Ltd. (Osaka, Japan) and used without further purification. Pure water was obtained by ion exchange and distillation equipment (Yamato).

2.2. Apparatus and procedures

A microwave irradiation apparatus containing high-pressure glass reactor was employed to perform the glucose isomerization experiments. The detail of the apparatus is given in previous reports [14,15]. Briefly, multi-mode microwave oven (m-reactor, Shikoku Keisoku, Co., Ltd.) was used to heat a high-pressure glass reactor (inner volume: 10 mL, maximum pressure: 10 MPa, Hiper glasstor, Takatsu Techne Co., Ltd.) The glass reactor was covered with polycarbonate outer tube and PEEK caps. A vacuum was used between the outer cover and the glass reactor to reduce heat losses by convection. Water was fed into the evacuated space to assist in the termination of the reaction after the reaction completed.

An aqueous solution (5 g) of glucose (2 wt%) and catalyst (0.1 g) were loaded into the glass reactor. After sealing the glass reactor, 1.3 MPa of nitrogen gas was introduced to inhibit solution boiling. For comparison, glucose reaction experiments without catalyst and with 10 mM of NaOH instead of pure water were conducted. The loaded reactor was placed in the microwave oven set at 120–180 °C and temperature was maintained at the settings for 3–30 min. After the reaction, the product solution consisting of the reactants, products, water and catalyst was recovered with rinsing the reactor by water after cooling and depressurization. Solid catalysts and water soluble products were separated by vacuum filtration.

2.3. Analysis and definition

Liquid products were analyzed by HPLC (column: Shodex SH1011, detector: RI, effluent: 1 mL/min of 5 mM H_2SO_4 sulfuric acid aqueous solution, column oven: 60 °C) and yields were defined on a molar basis. The detected components were glucose, fructose, 5-hydroxymethyl-furfural (5-HMF), glyceraldehyde, erythrose, glycoaldehyde, lactic acid, formic acid, acetic acid, and levulinic acid. In this study, the focus of the research was on glucose isomerization thus glucose yield, fructose yield and fructose selectivity (fructose yield/glucose conversion) were mainly evaluated (Fig. 1).

3. Results and discussion

3.1. Experimental data

Time profiles of glucose reactions are shown in Fig. S1 (Supplementary material). Glucose was relatively stable at 140–180 °C for 30 min and the maximum conversion was 23% at 180 °C for 30 min and then fructose yield was 7%. Fig. S2 shows the glucose reaction with 10 mM NaOH at 140 °C and 160 °C for 3–15 min. The maximum conversion was 30% and then fructose yield was about 20%. For both cases (without catalyst and with NaOH), glucose conversion and fructose yield reached a plateau that resembled chemical equilibrium. Fig. 2 shows the fructose selectivity against glucose conversion with and without NaOH. Without catalyst, fructose selectivity drastically dropped and the formation into the other products was formed with progressing glucose reaction. In the presence of NaOH, selectivity of glucose isomerization into fructose was enhanced, but the selectivity was still low with fructose