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Glucose reactions with acid and base catalysts in hot compressed water at 473 K

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Abstract—The effects of the homogeneous catalysts (H_2SO_4 and NaOH) and heterogeneous catalysts (TiO_2 and ZrO_2) on glucose reactions were examined in hot compressed water (473 K) by a batch-type reactor. From the homogeneous catalyst studies, we confirmed that the acid catalyst promoted dehydration, while isomerization of glucose to fructose was catalyzed by alkali. Anatase TiO_2 was found to act as an acid catalyst to promote formation of 5-hydroxymethylfuraldehyde (HMF). Zirconia (ZrO_2) was a base catalyst to promote the isomerization of glucose. The effects of the additives were also confirmed through fructose reactions.

Keywords: Glucose; HMF; Fructose; TiO_2; ZrO_2; Acid; Alkali

1. Introduction

Glucose, which is the monomer unit of cellulose, will be one of the most important starting chemicals in the coming society that is highly dependent on biomass. To develop a sustainable society using biomass resources, a highly selective glucose conversion process is strongly needed. Hot-compressed water, including hydrothermal and supercritical water (SCW) conditions, is quite a powerful reaction media for glucose conversion. Kabyemela et al.[1–4] proposed a number of primary reactions of glucose in SCW. Sinag et al.[5] suggested a simple but useful reaction pathway for glucose in SCW. According to these reaction mechanisms,[1–5] the main reaction pathways of glucose conversion in SCW were dehydration (namely C–O bond breaking) and C–C bond-breaking reactions (such as retro-aldol condensation). Unsaturated compounds such as furans and phenols are produced through dehydration and low molecular acids, aldehydes, and gaseous form via bond-breaking reactions.

Some researchers have reported controlling reactions of glucose in hot compressed water with or without a catalyst.[6–8] Goto et al.[6] and Sasaki et al.[7] studied glucose reactions in SCW at various temperatures and pressures without any catalyst using a flow apparatus. They suggested that dehydration (C–O bond splitting) was dominant at lower temperatures (523–623 K), while the retro-aldol condensation (namely C–C bond breaking) mainly occurred at higher temperatures (673–773 K). Above the critical temperature, dehydration of glucose was promoted with increasing pressure (water density). As summarized recently, at high temperature and low water density, radical reactions are likely to take place; on the other hand, ionic reactions mainly occur at low temperature and high water density.[9] One way to control glucose reactions is to change the temperature and pressure (water density). In particular, for ionic reactions, water density is the most important controlling factor in the absence of a catalyst. However, water density of the saturated liquid phase cannot be changed drastically with pressure below the critical point compared to the supercritical region. Thus, in sub-critical conditions of water, additives must be used to control ionic reactions.

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Among the dehydration products of glucose, 5-hydroxymethylfurfural (HMF) becomes remarkably important because it can be used as a monomer for useful polymers such as polyethylene terephthalate, or an intermediate for a medicinal purpose, and so on.[10] Though there are reactions that produce HMF at high yield from biomass, there are no processes for HMF production. This is mainly because of the use of strong acids and organic solvents such as DMSO, which require neutralization and additional separation during the process.[11] Thus, HMF is called a 'sleeping giant'.[12] Bicker et al.[12] studied the effect of acetone and H_2SO_4 on glucose conversion into HMF. A HMF selectivity of 48% was obtained by dehydration of glucose in a supercritical acetone (90 wt %)–water (10 wt %) solvent mixture with 10 mM H_2SO_4 at 453 K and 20 MPa. The C–O bond splitting of the C–OH group in alcohols, namely dehydration, was reported to be enhanced by adding acid catalyst in hot compressed water at a lower temperature.[13] Thus, the elimination of hydroxy groups in glucose was enhanced by an acid catalyst. However, from the viewpoint of green chemistry, the addition of a homogeneous acid catalyst and organic solvent is not consistent with the 'green' requirement of the process.

An alternate catalyst to an effective acid catalyst for organic reactions in hot compressed water is a metal oxide. Tomita et al.[14] employed an MoO_3/Al_2O_3 catalyst for the hydration of propene (hydration is also catalyzed by an acid catalyst) in sub- and supercritical water. They confirmed that MoO_3/Al_2O_3 can be used as an acid catalyst instead of H_2SO_4. Watanabe et al.[15] conducted formaldehyde reactions in SCW using metal oxides and reported that TiO_2 and MoO_3 behaved as acid catalysts for formaldehyde reactions. This same conclusion was reported for the study done on the dehydration of 2-propanol in supercritical water.[16]

In this study, the effects of some additives on glucose conversion were examined in hot compressed water, by a batch reactor. At first, homogeneous acid and alkali were added to examine the effect of protons on the reaction of glucose. Next, metal oxides (TiO_2 and ZrO_2) were used in the glucose reaction to understand the controllability of the glucose reaction by the metal oxides. Also, in order to confirm the effect of additives (homogeneous and heterogeneous catalysts) on the reaction, reactions starting from fructose were conducted.

2. Experimental

Glucose and fructose were obtained from Wako Pure Chemical and used as received. Sodium hydroxide (NaOH, 1 M aq solution) and sulfuric acid (H_2SO_4, 1 M aq solution) were purchased from Wako Pure Chemical and used as received. Titanium oxides (anatase and rutile TiO_2,) were obtained from Wako Pure Chemical and used without pretreatment. Zirconia (ZrO_2) was prepared by calcination of zirconium hydroxide, which was obtained from Nakalai Tesque, at 673 K for 3 h. The ZrO_2 was confirmed as a tetragonal–monoclinic mixture phase from XRD analysis. Pure water, which was distilled after deionization, was obtained with a water distillation apparatus (Yamato Co., model WG-220).

The reactions were carried out in an SS 316 stainless steel tube bomb reactor with an inner volume of 6 cm^3. The loaded amount of glucose was 0.1 g and that of water was 1.0 g. When the effect of homogeneous acid or alkali on the glucose reaction was examined, 1.0 g of the acid or alkali solution (1 mM) was loaded instead of pure water. The loaded amount of the metal oxides was always 0.1 g. Ar was loaded at 2.5 MPa to make easier the recovery of the gaseous product after the reaction. After the loading, the reactor was submerged into the heating bath. Quenching the reactor into water bath stopped the reaction. Reaction temperature was 473 K and reaction time ranged from 60 to 600 s. From preliminary studies, the heating period in the fluidized sand bath was 60 s.[17] The gas products were recovered and the composition was determined. However, in this study, the volumes of the gas products were always quite small, and thus no further analysis was performed. The reactor was opened and washed with pure water to recover the liquid samples. Char formation was sometimes observed; however, the amount of char was small and not analyzed further.

The identification and quantification of the product gas was conducted by GC–TCD (Shimadzu, model GC-7A, and Hitachi, model GC163). To understand the product distribution in the recovered solution, HPLC analyses were conducted with a KS-802 column. In this study, we focused on only isomerization and dehydration among the primary reactions, and the products of isomerization (fructose) and dehydration (1,6-anhydroglucose (AHG), HMF, and furfural) were quantified. The total amount of carbon in the recovered water solution was measured using the TOC (total organic carbon detector, Shimadzu, model TOC-5000 A).

Product yield (mol%) of carbon compound was evaluated from the carbon base as shown below:

$$\text{Product yield [mol\%]} = \frac{\text{An amount of carbon atom in a product}}{\text{The amount of carbon atom in the loaded glucose}} \times 100 \qquad (1)$$

3. Results and discussion

3.1. Without additive

The reaction time (including the heating period) was from 60 to 300 s. Gas and char formations were not

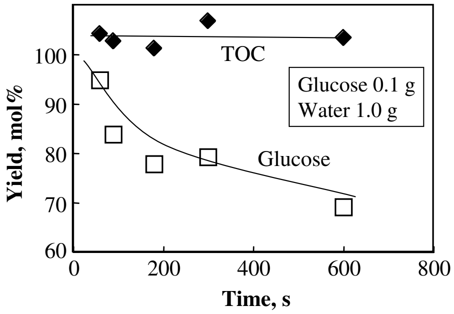

Figure 1. Yield of glucose and TOC without additive in hot compressed water at 473 K.

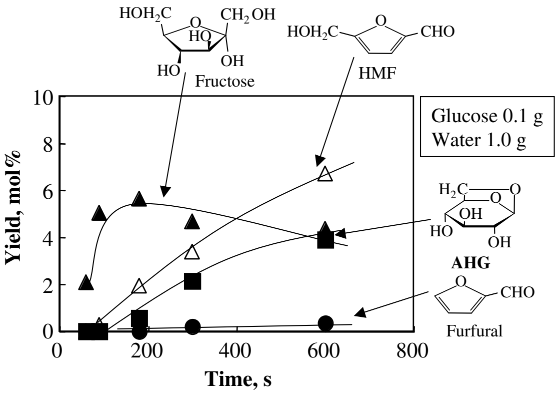

Figure 2. Yield of the liquid products in hot compressed water at 473 K.

observed. Figures 1 and 2 show the glucose conversion and the products that were identified and quantified (fructose, AHG, HMF, and furfural), respectively.

The values of TOC were always almost 100%. Glucose gradually converted (30% conversion at 600 s of reaction time), and the liquid products gradually formed with glucose conversion. As shown in Figure 2, fructose initially formed. HMF was obtained with disappearing fructose and AHG formed through the dehydration of glucose. At longer reaction time (after 300 s), furfural was obtained in a low yield (below 1 mol %). Figure 3 shows a simple reaction network of glucose in hot compressed water at 473 K. This pathway was based on the model by Kabyemela et al.,[1–4] Sinag et al.,[5] and Srokol et al.[8] Namely glucose isomerizes into fructose. Both glucose and fructose are dehydrated into AHG and HMF, respectively. Furfural is formed by the decomposition of ketose and C-5 monosaccharide, which are intermediates. These compounds also converted into acid/aldehyde/phenols/gas/char as suggested by Sinag et al.[5] and Watanabe et al.[18]

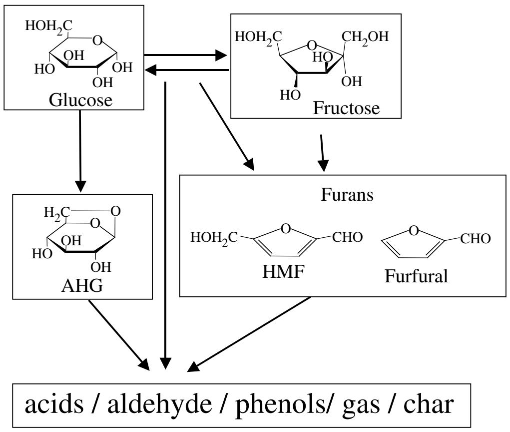

Figure 3. Reaction pathways of glucose in hot compressed water at 473 K.

3.2. With homogeneous catalysts

The glucose conversion and the TOC values are shown in Figure 4, and the yields of the liquid products (fructose, AHG, HMF, and furfural) are shown in Figure 5, with and without additive. The reaction time was 300 s. From all these reactions, the amounts of gaseous products were only trace amounts, and the result of the gaseous products are not shown here. From Figure 4, the conversion was promoted by adding the additives except for rutile TiO_2. As shown in Figure 5, fructose

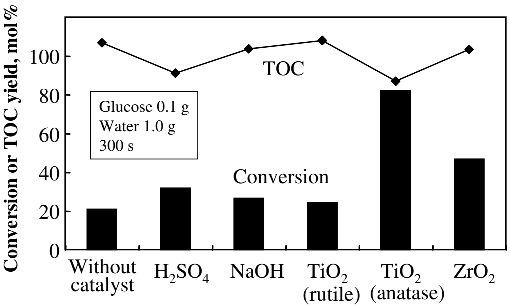

Figure 4. Effect of the additives on the conversion of glucose and the TOC value at 473 K and 300 s.

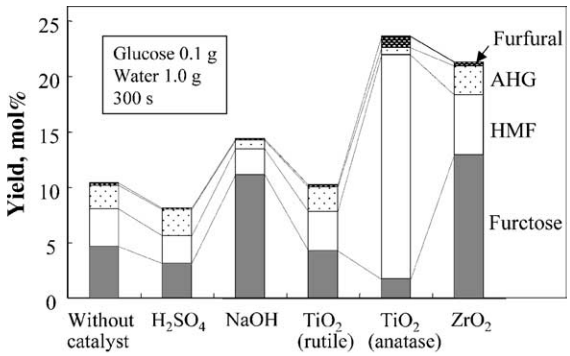

Figure 5. Effect of the additives on the yield of the liquid products at 473 K and 300 s.

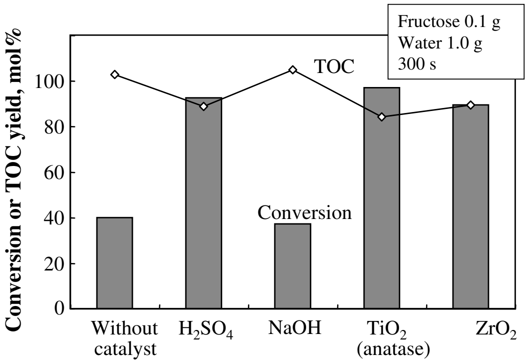

Figure 6. Effect of the additives on the conversion of fructose and the TOC value at 473 K and 300 s.

formation was inhibited by H_2SO_4, while the yields of HMF and AHG were not suppressed. In the case of addition of alkali NaOH, the conversion and the TOC value (Fig. 4) were almost the same as those without any catalyst. The addition of NaOH promoted the yield of fructose and inhibited the yield of AHG.

In order to understand the effect of the additives on glucose reactions in more detail, fructose conversions at 473 K and 300 s were conducted. Figure 6 shows the fructose conversion and TOC value in the absence and presence of the additives. Figure 7 shows the liquid product (glucose, HMF, and furfural) yield from the fructose conversion at 473 K and 300 s as a function of the additive. By adding the homogeneous acid, fructose conversion was enhanced and HMF formation was slightly promoted. On the other hand, in the presence of NaOH, fructose conversion was almost the same as without catalyst, and HMF formation was inhibited, and glucose was obtained.

Through these results, the effect of the homogeneous catalysts on glucose reactions were as follows: (1) promotion of isomerization between glucose and fructose is catalyzed by alkali,[19] and (2) promotion of dehydration of fructose is promoted by acid. Both the isomerizations of glucose into fructose (Fig. 5) and fructose into glucose (Fig. 7) are promoted in the alkali condition.[19] The equilibrium of the isomerization is quite important to develop the process of glucose conversion in hot compressed water. Kabyemela et al.[1] measured the kinetics of the epimerization of glucose. According to this report, the equilibrium favors fructose formation in SCW because the rate of isomerization of fructose into glucose is negligibly small compared to that of glucose into fructose. Under acidic conditions, HMF formation from fructose was slightly promoted (Fig. 7). A similar result was also reported by Antal et al.,[20] who found that the fructose yield (45%) from fructose in the presence of 2 mM H_2SO_4 was roughly two times higher than that without any catalyst (25%) in hot compressed water at (523 K and 34.5 MPa). Direct dehydration products (AHG from glucose and HMF from fructose) were not greatly enhanced by adding the acid (Figs. 4 and 6). Thus, the high conversion was probably related to the formation of intermolecular dehydration to form polymeric compounds (namely condensation) because the gaseous products were not enhanced by the addition of acid. Condensation is strongly dependent on the concentration of condensable materials such as glucose and fructose.[21] In this study, 0.56 M glucose or fructose was used as the starting materials. This concentration and the addition of acid may have possibly led to the promotion of condensation reactions. A lower concentration of the starting material may be favored to promote monomolecular dehydration (AHG from glucose and HMF from fructose), and this possibility will be examined in the near future. The effects of homogeneous acid and alkali on glucose reactions are suggested as shown in Figure 8.

3.3. With heterogeneous catalysts

As shown in Figures 4 and 5, rutile TiO_2 has no significant effect on glucose reactions under these conditions.

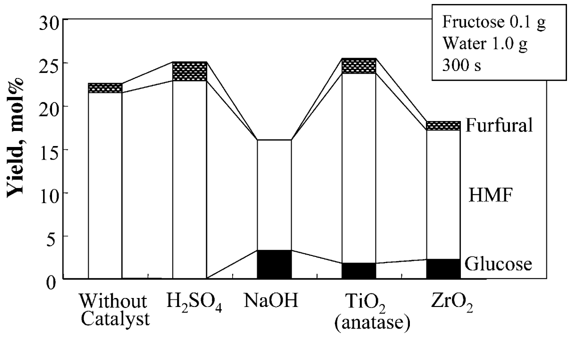

Figure 7. Effect of the additives on the yield of the liquid products at 473 K and 300 s.

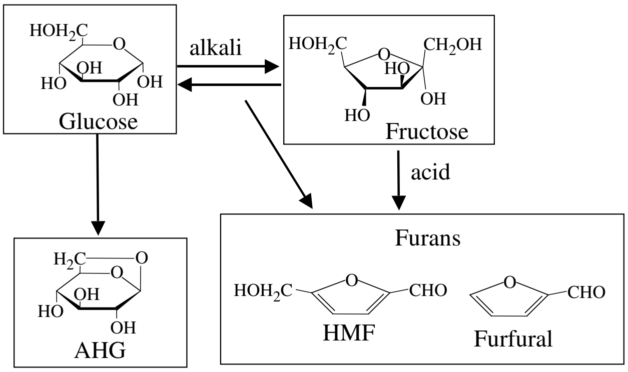

Figure 8. Effects of the homogeneous catalysts on glucose primary reactions at 473 K.

ZrO_2 catalyst apparently acts as a base catalyst as shown in Figures 4–7. That is, isomerization of glucose and fructose was catalyzed by NaOH and ZrO_2. In the presence of anatase TiO_2, glucose conversion was significantly enhanced (Fig. 4), and the HMF yield was remarkably high (Fig. 5). Anatase TiO_2 enhanced fructose conversion (Fig. 6) and the HMF yield (Fig. 7). These effects of anatase TiO_2 on glucose and fructose conversions show that anatase TiO_2 can be considered as an acid catalyst.

The acidic and basic characteristics of these catalysts (anatase TiO_2 and ZrO_2) on glucose and fructose reactions were also consistent with the study we preformed previously on formaldehyde reactions.[15] That is, anatase TiO_2 was an acid and ZrO_2 was a base for formaldehyde reactions. The results of this study and the formaldehyde reactions suggest that the function of the metal oxide as an acid and base catalyst can be applied for various other organic reactions.

In a previous paper,[15] we reported that the acidity and basicity of metal oxides such as TiO_2 and ZrO_2 can be roughly estimated from the electronegativity of the metal ion. However, in this study and in the formaldehyde study,[14] anatase and rutile TiO_2 show different catalytic activities. Namely, rutile TiO_2 is always inactive. Thus, the estimation of catalytic activity from the electronegativity of the metal ion may not be universal. One example is Al_2O_3. The most stable state of Al_2O_3, α-Al_2O_3, is an inactive species for various organic reactions; however, the transition state of Al_2O_3 such as γ-Al_2O_3 have an acid on the surface that makes it active.[22] Also, monoclinic ZrO_2 and tetragonal ZrO_2 show a different acidity and basicity.[23]

We observed a difference between the heterogeneous acid catalyst (anatase TiO_2) and the homogeneous acid catalyst (H_2SO_4) we used. The isomerization of fructose to glucose proceeded in the presence of anatase TiO_2 while it did not in the presence of H_2SO_4, as shown in Figure 7. On the other hand, this isomerization was catalyzed by alkali NaOH (Figs. 5 and 7). This result implies that the heterogeneous acid catalyst, anatase TiO_2, has also a basic site to enhance fructose isomerization to glucose. This bifunctionality is one of the advantages of using of the metal oxide as a catalyst.

Figures 9 and 10 show the time profiles of glucose conversion and product distribution, respectively, with anatase TiO_2. Glucose conversion was significantly enhanced by adding anatase TiO_2 as shown in Figure 9. With the enhancement of glucose conversion, consumption of fructose was promoted, as shown in Figure 10. AHG continuously formed within the reaction time without a catalyst as shown in Figure 2, while its yield with anatase TiO_2 gradually decreased in the reaction time (Fig. 10). HMF and furfural formation were also increased by adding anatase TiO_2. The yield of furfural was always below 1 mol %. Anatase TiO_2 selectively enhanced HMF formation from glucose. According to the concept shown in Figure 8, HMF formation is produced from fructose and the intermediate products of the isomerization between glucose and fructose. These results (Figs. 7 and 10) indicate the main reaction for HMF formation in the presence of anatase TiO_2 is not a reaction that includes fructose. As shown in Figure 7, the isomerization of fructose into glucose was promoted by anatase TiO_2. Also, as shown in Figure 10, fructose decreased rapidly within the reaction time. This indicates that the isomerization of glucose into fructose occurred in a shorter reaction time (before 60 s), and fructose was rapidly consumed after 60 s. These results suggest that the increase of HMF formation by anatase TiO_2 is related to the intermediate compounds during isomerization. The intermediate products of the isomerization between glucose and fructose are ring-opened compounds that are not stable.[2] The acidic sites on the surface of anatase TiO_2 might promote the dehydration of the intermediate. Thus, acidic and basic sites on the surface of anatase TiO_2 promoted HMF formation from glucose in hot compressed water. In conclusion, the effect of anatase TiO_2 on glucose in hot compressed water at 473 K is suggested as shown in Figure 11.

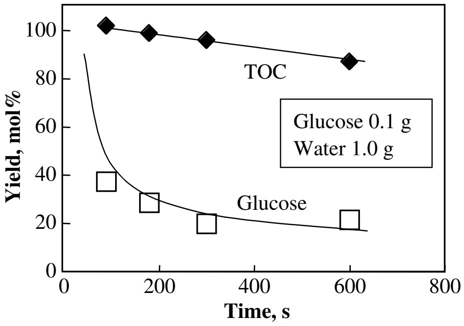

Figure 9. Yield of glucose and TOC with anatase TiO_2 in hot compressed water at 473 K.

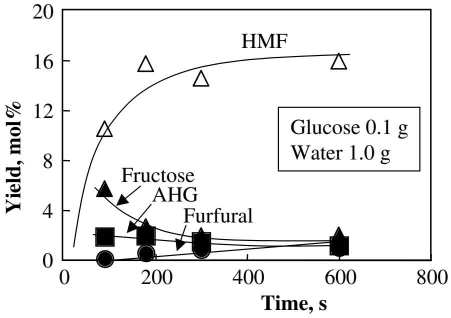

Figure 10. Yield of the liquid products with anatase TiO_2 in hot compressed water at 473 K.

Now, we are studying the catalytic activity of anatase TiO_2 by the use of TPD. Also, exploration of more

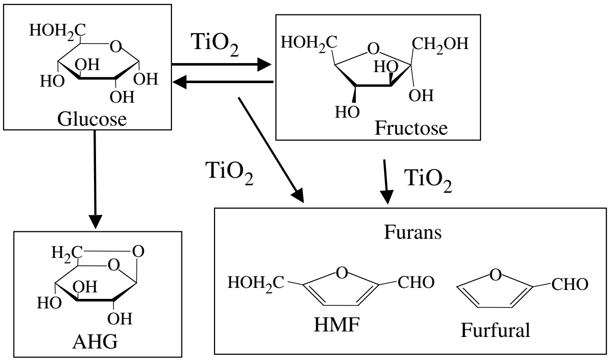

Figure 11. Effects of anatase TiO$_2$ on glucose primary reactions at 473 K.

effective catalysts and optimum conditions to produce HMF from glucose are being studied.

4. Conclusion

We examined the effect of additives on the reactions of glucose and fructose in hot compressed water at 473 K. The addition of alkali promoted isomerization of glucose and fructose. Because this phenomenon was observed in the presence of ZrO$_2$, ZrO$_2$ was considered as a base catalyst for the glucose and fructose reactions. The addition of homogeneous acid (H$_2$SO$_4$), dehydration and condensation was promoted. The addition of anatase TiO$_2$ also promoted dehydration and condensation reactions. Thus, it is an acid catalyst. Furthermore, anatase TiO$_2$ acted as a base catalyst for the fructose reaction. These dual characters of acidity and basicity of anatase TiO$_2$ may be the reason for the high yield of HMF from glucose.

Acknowledgements

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