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Sonication assisted rehydration of hydrotalcite catalyst for isomerization of glucose to fructose

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ABSTRACT

A series of hydrotalcite catalysts, including mother hydrotalcite (HT_M), calcined hydrotalcite (HT_C), and rehydrated hydrotalcites (HT_RM and HT_RSX) were prepared for isomerization of glucose to fructose. Two types of rehydration methods such as mechanical stirring method and sonication assisted method were employed for rehydration of hydrotalcite. Structure of hydrotalcite was successfully recovered to a layered double hydroxide structure via two rehydration processes (Memory effect of hydrotalcite). All rehydrated hydrotalcites (HT_RS*X*) with a sonication assisted method exhibited a higher fructose yield than rehydrated hydrotalcite (HT_RM) with a vigorous mechanical stirring in this reaction. In consideration of catalytic activity and rehydration time, sonication rather than mechanical stirring played an efficient role to improve catalytic activity of hydrotalcite in this reaction. Characterization results clearly revealed that the enhanced catalytic activity of HT_RS*X* catalyst was due to its abundant surface weak base sites resulted from a facile vertical breaking and exfoliation of hydrotalcite layers during the sonication assisted rehydration process. Yield for fructose over rehydrated hydrotalcite catalysts showed a tendency to increase with decreasing the crystallite size of catalyst and with increasing the weak base sites of catalyst. Among the catalysts tested, HT_RS10 with the smallest crystallite size and the largest weak base sites exhibited the highest fructose yield in this reaction.

1. Introduction

The rapid depletion of fossil fuels such as coal and crude oil has resulted in increased utilization of renewable energy [1–5]. Biomass represents one of the promising renewable energy sources, because bioenergy can help in reducing the oil dependency and fossil-based greenhouse gas emission [6–9]. Biomass is all biologically-produced organic materials derived from recently living organisms, including plants, animals, and their by-products. There are two ways to use biomass as an energy source. One is a direct combustion to produce heat, and the other is an indirect converting biomass to various forms of biofuels or valuable chemicals [10,11].

In biomass converting technologies, glucose has been considered as a key material. Glucose is used as a main energy source in most organisms (from bacteria to humans), so that it can be biologically converted to various chemicals. In other words, glucose is a platform chemical in producing biomass-derived chemicals [12,13]. However, biological conversion of glucose using enzyme has various drawbacks: (i) limiting operating temperature range, (ii) high-purity reactant, (iii) short life time of enzyme compared to inorganic catalyst, (iv) high operating cost for mass production [14–16]. Therefore, many researchers have extensively investigated glucose conversion reactions over inorganic catalysts with an aim of synthesizing valuable chemicals from glucose such as fructose, lactic acid, glyceric acid, and glyceraldehyde [17,18].

Fructose is commonly added to foods and drinks for palatability and taste enhancement due to its low cost and high sweetness. In addition, fructose can be used as a starting material for the synthesis of value-added chemicals (e.g., 5-hydroxymethylfurfural, levulinic acid, furandicarboxylic acid, dimethyl furan, and dihydroxymethylfuran) [19,20]. Therefore, isomerization of glucose to fructose is one of the important processes in biomass converting technologies. Although biological isomerization of glucose to fructose using xylose isomerase is industrially operated, as already mentioned, the biological process has many disadvantages over the chemical process. In this respect, we attempted to produce fructose form glucose via isomerization reaction over inorganic catalyst in this study.

Base catalysts are well-known to be efficient for isomerization of glucose to fructose [21]. Among various base catalysts,

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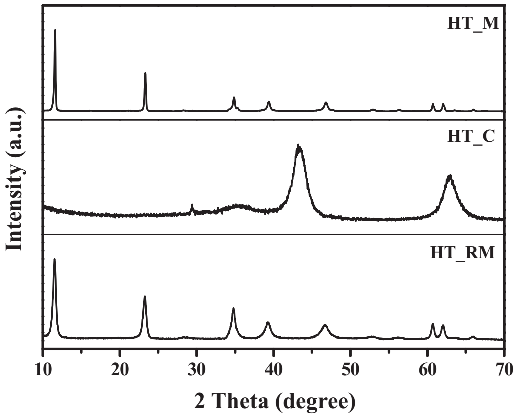

Fig. 1. XRD patterns of mother hydrotalcite (HT_M), calcined hydrotalcite (HT_C), and rehydrated hydrotalcite (HT_RM) catalysts.

hydrotalcite was chosen as a base catalyst for isomerization reaction of glucose in this study. Hydrotalcites are one of the layered double hydroxide (LDH) clays with a general formular of $[M^{II}{}_{1-x}M^{III}{}_{x}(OH_2)][A^{n-}{}_{x/n}\cdot mH_2O]$. Here, M^{II} and M^{III} are divalent and trivalent metal cations, respectively. Also, A^{n-} represents compensating anion located in the interlayer space [22–25]. It is noteworthy that hydrotalcite has a well-known memory effect. Hydrotalcite can be changed into mixed metal oxide with a spinel structure via thermal decomposition under air atmosphere (calcination), and then, the mixed metal oxide can be reconstructed to original hydrotalcite with a layered double hydroxide structure by immersion in water (rehydration) [26–28]. A further important consideration is that base properties of hydrotalcite can be different through rehydration process. It was revealed in our previous work that rehydrated hydrotalcite served an efficient catalyst for isomerization of glucose to fructose [8]. The enhanced catalytic activity of rehydrated hydrotalcite compared original hydrotalcite was due to its abundant weak base sites formed by vertical breaking and exfoliation of layers in the hydrotalcite structure during the rehydration process.

Sonication has been considered as a realizable technique for particle size reduction of clay [29,30]. The sonication can give a shock-wave impact on the surface and interlayer of clays, which can result in particle size reduction of clays [31–33]. In this work, therefore, sonication assisted rehydration of hydrotalcite was conducted to facilitate vertical breaking and exfoliation of hydrotalcite layers during the rehydration process. A series of rehydrated hydrotalcites with different sonication time were prepared by a sonication assisted rehydration method. For a comparison, rehydrated hydrotalcite by a mechanical stirring method was also prepared. The rehydrated hydrotalcites were characterized by XRD and FE-SEM analyses. Base properties of rehydrated hydrotalcites were determined by titration experiments. Effect of sonication assisted rehydration on the catalytic performance of hydrotalcite in the isomerization of glucose to fructose was investigated. Finally, correlation between catalytic activity of rehydrated hydrotalcite and its crystallite size or base property was also studied.

Table 1
Catalytic performance of HT_M, HT_C, and HT_RM catalysts in the isomerization of glucose to fructose at 100 °C after a 3 h-catalytic reaction.

Catalyst	Conversion of glucose (%)	Selectivity for fructose (%)	Yield for fructose (%)
HT_M	9.3	57.9	5.4
HT_C	20.1	68.1	13.7
HT_RM	39.1	78.6	30.8

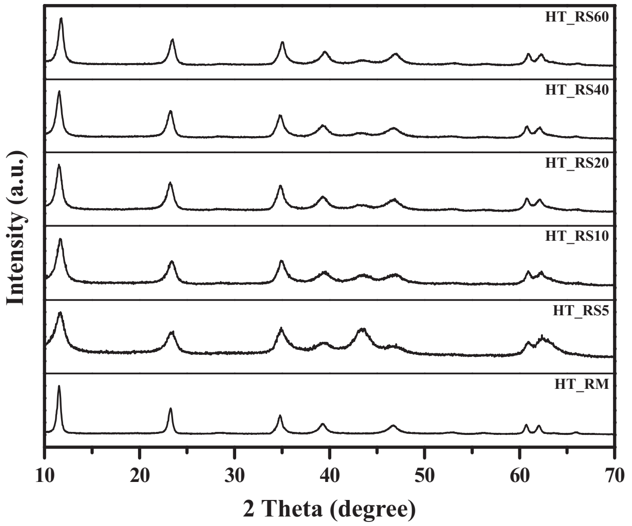

Fig. 2. XRD patterns of rehydrated hydrotalcites (HT_RS*X*) with different sonication time (*X*).

2. Experimental

2.1. Catalyst preparation

Mg-Al hydrotalcite (HT_M) with a ratio of Mg/Al = 3 was purchased as a mother catalyst from Sigma–Aldrich. The provided catalyst was calcined at 450 °C during 10 h under an air stream to obtain the calcined Mg-Al hydrotalcite (HT_C). The calcined catalyst was rehydrated in decarbonated water under nitrogen atmosphere by two methods: (i) with a vigorous mechanical stirring at 60 °C for 24 h, (ii) with a sonication at 60 °C for desired time (5, 10, 20, 40, and 60 min). The rehydrated samples were obtained by filtrations. The obtained solid product was finally dried overnight at 80 °C to yield the rehydrated hydrotalcite. The rehydrated hydrotalcite under vigorous mechanical stirring without sonication was denoted as HT_RM. In addition, the hydrotalcites rehydrated using sonication assisted rehydration were represented by HT_RS*X*, where *X* represents sonication time in minutes.

2.2. Catalyst characterization

Crystal structures of the prepared catalysts (HT_M, HT_C, HT_RM, and HT_RS) were analyzed by XRD measurements (Shimadzu, XRD-7000) using Cu-Kα radiation (λ = 1.54056 Å) operated 40 kV and 40 mA. SEM analysis (Jeol, JSM-6700F) was carried out to examine the surface morphology of the catalysts. Surface area of the catalysts was determined using a BET apparatus (BEL Japan, BELSORP-max).

Base properties of the catalysts were determined using the irreversible adsorption of noninteracting organic acids, according to the similar method in the literature [25]. Phenol ($pK_a = 9.9$) was used as a probe molecules to measure the strong basicity of the

Table 2
Crystallite size of the catalysts calculated by Scherrer equation.

Catalyst	Crystallite size (nm)	
	0 0 3	1 1 0
HT_M	44.5	30.5
HT_RM	18.7	22.7
HT_RS5	7.6	13.6
HT_RS10	9.6	16.8
HT_RS20	11.3	19.7
HT_RS40	13.2	20.5
HT_RS60	13.6	22.2

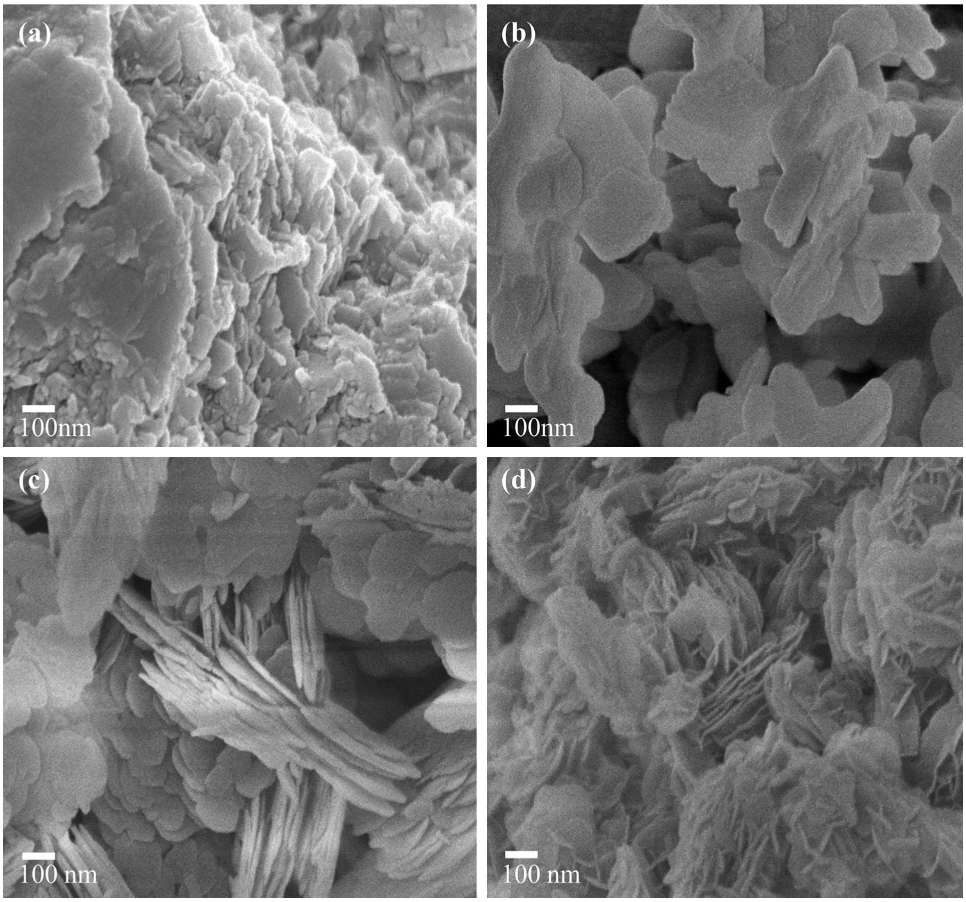

Fig. 3. SEM images of (a) mother hydrotalcite (HT_M), (b) calcined hydrotalcite (HT_C), and rehydrated hydrotalcites ((c) HT_RM and (d) HT_RS10).

sample. A strong acid as acrylic acid (pK_a = 4.3) was also employed to probe the total basicity of the sample. The number of weak base sites was calculated by subtracting strong basicity from total basicity. Prior to the basicity measurement, all catalysts were pretreated overnight at 60 °C under static air condition to remove any physisorbed organic molecules. 0.05 g of the pretreated sample was charged into the stoppered bottle, and then, 10 ml of standard solution of organic acid (phenol/acrylic acid) in cyclohexane was also added to the bottle. The resulting solution was thoroughly mixed for 2 h at room temperature. In order to avoid the interacting of the sample with atmospheric CO_2 and water, the expose of the sample to atmosphere was minimized. In all experiments, 2 h is found to be enough to achieve equilibrium condition at room temperature. Concentration of the non-adsorbed organic acid in solution was determined by UV–vis spectrometer (Sinco, S-3100). Calibration curves derived from standard solutions were employed for the calculation. From these results, concentration of the adsorbed organic acid, and subsequently, basicity of the sample were finally obtained.

2.3. Isomerization of glucose to fructose

Isomerization of glucose to fructose was conducted in a batch-type glass reactor. 0.3 g of glucose, 0.1 g of catalyst, and 10 ml of dimethylformamide were used for a typical reaction. The reaction was performed at 100 °C for 3 h. After the reaction was completed, the reactor was cooled in an ice bath. The catalysts were filtered off using syringe filter and the filtrate was analyzed by high performance liquid chromatography (Young Lin instrument, YL 9100) equipped with an ultraviolet–visible (UV–vis) detector and a refractive index (RI) detector. 0.005 M H_2SO_4 was used as a mobile phase and reaction products were separated using a Biorad Aminex HPX87H column. Conversion of glucose and selectivity for fructose were determined using the following equations. Yield for fructose was calculated by multiplying conversion and selectivity.

$$\text{Conversion of glucose}\,(\%) = \frac{\text{moles of glucose reacted}}{\text{moles of glucose supplied}} \times 100$$

$$\text{Selectivity for fructose}\,(\%) = \frac{\text{moles of fructose formed}}{\text{moles of glucose reacted}} \times 100$$

3. Results and discussion

3.1. Memory effect of hydrotalcite catalyst

Memory effect of hydrotalcite catalyst was confirmed by XRD measurements (Fig. 1). Purchased hydrotalcite (HT_M), which used as a mother catalyst in this work, showed the characteristic XRD

Table 3
Catalytic performance of rehydrated hydrotalcites (HT_RM and HT_RSX) in the isomerization of glucose to fructose at 100 °C after a 3 h-catalytic reaction.

Catalyst	Conversion of glucose (%)	Selectivity for fructose (%)	Yield for fructose (%)
HT_RM	39.1	78.6	30.8
HT_RS5	43.8	78.7	34.5
HT_RS10	41.5	88.0	36.6
HT_RS20	40.2	88.8	35.7
HT_RS40	39.6	86.4	34.3
HT_RS60	39.8	85.4	34.0

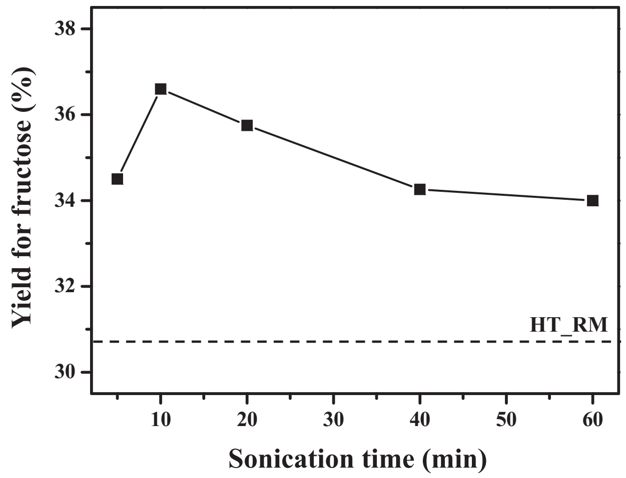

Fig. 4. Yield for fructose over HT_RS*X* catalysts in the isomerization of glucose to fructose at 100 °C after a 3 h-catalytic reaction, plotted as a function of sonication time (*X*).

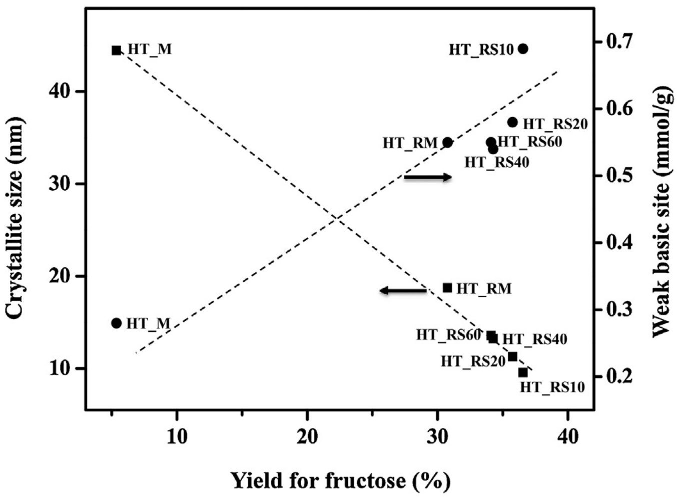

Fig. 5. Comprehensive correlations between yield for fructose, crystallite size, and weak base sites.

peaks of hydrotalcite materials. Concretely, the peaks corresponding to the basal planes ((0 0 3), (0 0 6), and (0 0 9) at $2\theta = 11.6^\circ$, 23.3°, and 34.8°, respectively) and those for the nonbasal planes ((1 1 0) and (1 1 3) at $2\theta = 60.7^\circ$ and 62.0°, respectively) were observed in the HT_M catalyst. This means that HT_M catalyst retained a layered double hydroxides structure, which is the characteristic structure of hydrotalcite [23]. Hydrotalcite calcined under an air stream (HT_C) showed a spinel structure of Mg-Al oxide, in good agreement with the previous reports [23,24]. It is noteworthy that rehydrated hydrotalcite (HT_RM) with a vigorous mechanical stirring exhibited the characteristic XRD peaks of hydrotalcite, indicating that the layered double hydroxides structure was recovered by the rehydration process. XRD results clearly showed that hydrotalcite could be successfully rehydrated in decarbonated water with a vigorous mechanical stirring. As shown in Fig. 1, HT_RM catalyst retained a broader XRD peaks for (0 0 3) and (1 1 0) planes than HT_M catalyst. As reported in our previous work [8], rehydration of hydrotalcite resulted in a smaller crystallite size formed by vertical breaking and exfoliation of layered structure.

Catalytic performance of hydrotalcite catalysts (HT_M, HT_C, and HT_RM) in the isomerization of glucose to fructose was summarized in Table 1. The catalytic activity was obtained at the reaction temperature of 100 °C after a 3 h-catalytic reaction. As expected, HT_RM catalyst showed a much better catalytic activity than HT_M catalyst in this reaction. This means that rehydration is an efficient method to improve catalytic activity of hydrotalcite in the isomerization of glucose to fructose. In our previous work [8], it was revealed that the weak base sites of hydrotalcite catalyst were responsible for this reaction. Therefore, main reason for the enhanced catalytic activity of HT_RM catalyst is thought to be a more abundant base sites of HT_RM formed by vertical breaking and exfoliation of layered structure during the rehydration process.

Table 4
Basicity of the catalysts (HT_M, HT_RM, and HT_RS*X*).

Catalyst	Base sites		
	Total base site (mmol/g)[a]	Strong base site (μmol/g)[b]	Weak base site (mmol/g)[c]
HT_M	0.28	1.058	0.279
HT_RM	0.55	4.976	0.545
HT_RS10	0.69	4.668	0.685
HT_RS20	0.58	4.881	0.575
HT_RS40	0.54	4.144	0.536
HT_RS60	0.55	4.530	0.545

[a] Acrylic acid was used as a probe molecular.
[b] Phenol was used as a probe molecule.
[c] Weak base site = Total base site – Strong base site.

3.2. Sonication assisted rehydration of hydrotalcite

Sonication assisted rehydration of hydrotalcite was employed to improve the catalytic activity of rehydrated hydrotalcite in the isomerization of glucose to fructose. A series of rehydrated hydrotalcites (HT_RS*X*) with different sonication time (*X*) were prepared. Fig. 2 shows the XRD patterns of HT_RS*X* catalysts. For comparison, the XRD pattern of rehydrated hydrotalcite (HT_RM) with a vigorous mechanical stirring was also represented in Fig. 2. Most of rehydrated hydrotalcites (HT_RS*X*) with a sonication assisted rehydration retained layered double hydroxides structures of hydrotalcite, indicating that HT_RS*X* catalysts were successfully rehydrated by a sonication assisted rehydration method. The XRD peaks corresponding to spinel structure of Mg-Al oxide was found in the HT_RS5 catalyst. It is inferred that 5 min was not enough to rehydrate hydrotalcite using a sonication assisted rehydration, leading to a mixed phase of layered double hydroxides structure and spinel structure in the HT_RS5 catalyst.

In order to confirm the effect of sonication assisted rehydration, the crystallite size of hydrotalcites was calculated by Scherrer equation using the XRD peaks for the (0 0 3) and (1 1 0) planes. Crystallite size of rehydrated hydrotalcites was listed in Table 2. Rehydrated hydrotalcites (HT_RM and HT_RS*X*) retained a smaller crystallite size than their mother catalyst (HT_M). Once again, we confirmed that vertical breaking and exfoliation of layers structure in the hydrotalcite were occurred during the rehydration process. Interestingly, a smaller crystallite size was found in all HT_RS*X* catalysts rather than HT_RM catalyst. This means that sonication facilitated the vertical breaking and exfoliation of layers structure during the rehydration of hydrotalcite, leading to the abundant surface base sites of HT_RS*X*. Therefore, it is expected that HT_RS*X* catalyst may show a better catalytic activity than HT_RM in isomerization of glucose to fructose.

Surface morphology of hydrotalcite catalysts was observed by SEM analysis. Mother hydrotalcite (HT_M) and rehydrated hydrotalcites (HT_RM and HT_RS10) retained layered structures, while a typical surface morphology for mixed metal oxide was observed in HT_C catalyst (Fig. 3). It is interesting to note that layered double hydroxide structure was more developed in the rehydrate hydrotalcites (HT_RM and HT_RS10) than mother hydrotalcite (HT_M).

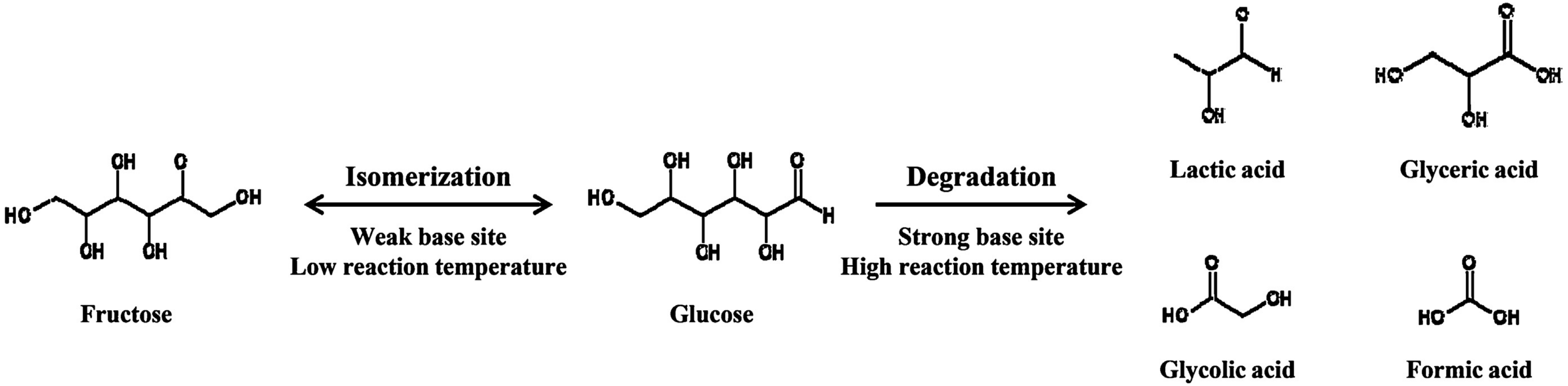

Fig. 6. Reaction pathway of glucose over base catalyst [8].

Especially, it was revealed that HT_RS10 (Fig. 3(d)) retained a more developed layered structure and a smaller crystallite size in comparison with HT_RM (Fig. 3(c)). In addition, BET surface areas of HT_M, HT_C, HT-RM, and HT_RS were found to be 2.6, 34.8, 30.6, and 37.9 m^2/g, respectively. These results were consistent with those obtained from XRD analysis. Therefore, sonication assisted rehydration is thought to be an efficient way to obtain more abundant surface base sites of hydrotalcite by the developed layered structure and the small crystallite size.

Catalytic activity of rehydrated hydrotalcites (HT_RS*X*) with a sonication assisted rehydration was investigated by conducting the isomerization of glucose to fructose at 100 °C. The obtained catalytic activity after a 3 h-catalytic reaction was summarized in Table 3. Results of rehydrated hydrotalcites (HT_RM) with a vigorous mechanical stirring were also listed as a reference. Conversion of glucose over the HT_RS*X* catalysts was higher than that over the HT_RM catalyst. In respect to the HT_RS*X* catalysts, conversion decreased with increasing sonication time (*X*). It is thought that conversion of glucose over rehydrated hydrotalcite catalysts may be closely related to its crystallite size. It can be inferred from catalytic activity (Table 3) and crystallite size (Table 2) that conversion of glucose increased with decreasing crystallite size of rehydrated hydrotalcite. HT_RS5 with the smallest crystallite size showed the highest conversion of glucose in this reaction. However, selectivity for fructose over the HT_RS*X* catalysts exhibited a different trend compared to conversion of glucose. Except for the HT_RS5, selectivity for fructose was almost the same in all HT_RS*X* catalyst. A low selectivity was particularly observed in the HT_RS5 catalyst. HT_RS5 retained a mixed phase of layered double hydroxides structure and spinel structure due to the insufficient sonication time (Fig. 2), leading to facile side reactions by the spinel structure of Mg-Al oxide. Consequently, yield for fructose, calculated by multiplying conversion and selectivity, was the highest over HT_RS10 catalyst. This means that appropriate sonication time is required for high catalytic activity of rehydrated hydrotalcite in the glucose isomerization reaction.

We plotted the yield for fructose over the HT_RS*X* catalysts with respect to sonication time (*X*), with an aim of confirming the effect of sonication rehydration method on the catalytic performance of hydrotalcite in this reaction. As shown in Fig. 4, all rehydrated hydrotalcites (HT_RS*X*) with a sonication assisted method exhibited better catalytic activities than rehydrated hydrotalcite (HT_RM) with a vigorous mechanical stirring. In consideration of catalytic activity and rehydration time, sonication was a good method for rehydration of hydrotalcite to improving its catalytic activity in isomerization of glucose to fructose. Yield for fructose over the HT_RS*X* catalysts showed a volcano-shaped curve with respect to sonication time (*X*). As expected, the maximum yield was obtained by the HT_RS10 catalyst.

3.3. Effect of basicity on the catalytic activity of rehydrated hydrotalcite

It is generally accepted that base property of the catalyst is responsible for isomerization of glucose to fructose. In order to verify the effect of base property on the catalytic activity of rehydrated hydrotalcite in this reaction, irreversible adsorption of noninteracting organic acid such as phenol and acrylic acid was conducted. HT_RS5 catalyst was excluded in this experiment due to its mixed phase of layered structure and spinel structure. The determined basicity of rehydrated hydrotalcites was summarized in Table 4. Total basicity was examined by acrylic acid adsorption, while strong basicity was measured by phenol adsorption. Weak basicity was calculated by difference in strong basicity and total basicity. Many researchers agree that weak base site of the catalyst plays a key role in isomerization of glucose to fructose. According to our previous work [8], glucose isomerization reaction is facilitated by weak base site of the catalyst at low temperature, while glucose degradation reaction is accelerated by strong base site of the catalyst at high temperature (Fig. 5). Therefore, we focused on the weak basicity of rehydrated hydrotalcite catalyst in this work.

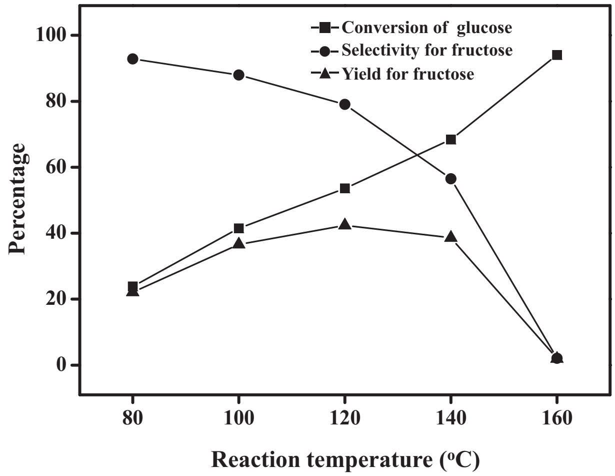

Fig. 7. Catalytic performance of HT_RS10 in the isomerization of glucose to fructose after a 3 h-catalytic reaction, plotted as a function of reaction temperature.

As listed in Table 4, weak basicity of the rehydrated hydrotalcite was different depending on the rehydration method and time. Rehydrated hydrotalcites (HT_RM and HT_RS*X*) retained more weak base sites than their mother catalyst (HT_M). This indicates that rehydration was an efficient method to increase the weak basicity of hydrotalcite catalyst. In particular, sonication assisted rehydration rather than mechanical stirring rehydration was more favorable for obtaining abundant weak base sites. Weak base sites of hydrotalcite catalysts roughly increased with decreasing their crystallite size (Tables 2 and 4). Among the catalysts tested, HT_RS10 with the smallest crystallite size retained the largest weak base sites.

From the characterization and activity of the hydrotalcite catalyst, it can be inferred that catalytic activity of hydrotalcite in glucose isomerization reaction may be closely related to its crystallite size and weak basicity. In order to confirm these results, correlation plots between yield for fructose (from Table 3), crystallite size calculated using the XRD peak for the (0 0 3) plane (from Table 2), and weak base sites (from Table 4) were obtained. As shown in Fig. 6, yield for fructose showed a tendency to increase with decreasing the crystallite size of catalyst and with increasing the weak base sites of catalyst. It was again confirmed that the crystallite size and the weak basicity of catalyst played a crucial factor determining the catalytic activity of hydrotalcite in this reaction. HT_RS10 with the smallest crystallite size and the largest weak base sites exhibited the highest fructose yield in this reaction. Sonication assisted rehydration served an efficient method to improve catalytic activity of rehydrated hydrotalcite due to its abundant surface weak base sites formed by a facile vertical breaking and exfoliation of hydrotalcite layers during the rehydration process.

3.4. Effect of reaction temperature

Effect of reaction temperature on the catalytic activity of rehydrated hydrotalcite was examined. For this purpose, HT_RS10 was chosen as a model catalyst, and then, the glucose isomerization reaction was conducted in the reaction temperature range of 80–160 °C (Fig. 7). Glucose conversion increased with increasing reaction temperature (kinetic effect), while fructose selectivity decreased with increasing reaction temperature (thermodynamic effect). As shown in Fig.6, high reaction temperature is unfavorable for producing fructose in glucose transformation reaction. As a result, fructose yield over the HT_RS10 catalyst was confirmed to be a volcano-shaped curve with respect to reaction temperature. The compensation between thermodynamic effect and kinetic effect led to a volcano-shaped curve of fructose yield with respect to reaction temperature.

4. Conclusion

Hydrotalcite catalyst was successfully rehydrated using two methods (mechanical stirring method and sonication assisted method). Memory effect of hydrotalcite through the calcination and rehydration process was well confirmed by XRD and SEM analyses. Rehydrated hydrotalcites retained a layered double hydroxide structure, which is a structure of original mother hydrotalcite. Rehydrated hydrotalcites showed a better catalytic activity than mother hydrotalcite in the isomerization of glucose to fructose, indicating that rehydration is an efficient method to improve catalytic activity of hydrotalcite in this reaction. Particularly, all rehydrated hydrotalcites (HT_RS*X*) with a sonication assisted method showed better catalytic activities than rehydrated hydrotalcite (HT_RM) with a vigorous mechanical stirring. When considering catalytic activity and rehydration time, sonication was a good way for rehydration of hydrotalcite to improving its catalytic activity in this reaction. Yield for fructose over HT_RS*X* catalysts showed a volcano-shaped curve with respect to sonication time (*X*). Among the catalysts tested, HT_RS10 showed the highest yield for fructose. The enhanced catalytic activity of HT_RS10 was attributed to its abundant surface weak base sites formed by a facile vertical breaking and exfoliation of hydrotalcite layers during the sonication assisted rehydration process.

Acknowledgments

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