

Mg-Al hydrotalcites as solid base catalysts for transformation of glucose to fructose

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Abstract

In this research, Mg-Al hydrotalcite compounds (HTs) are fabricated by constant pH at low supersaturation method. The prepared HTs act as solid base catalysts for the transformation of glucose to fructose in water medium. The activities of catalysts are monitored versus reaction temperature and time to find the optimum conditions. Under 120 °C and 20 min, the best catalyst is HT5 with maximum fructose yield of 16.3 %. The HT5 catalyst is tested for the heterogeneous nature and recyclability. The obtained results show that HT5 is true solid base catalyst. HT5 can be recovered easily and reuse several times with slight decrease in its activity. The deposition of organic residue on the surface of HT5 grains is blamed for the depletion of catalytic activity. In the regeneration process, HT5 undergoes a thermal treatment at 500 °C for 4 h in air to remove completely the contaminations. During that process, HT5 disassociates into MgO and Al₂O₃ before reconstruction stage in water medium to come back original structure of hydrotalcite. The reconstruction of HT5 can repeat many times proving that hydrotalcites are structure-memory materials. The activity of regenerated HT5 can be comparable to that of fresh catalyst.

Keywords. Glucose, fructose, isomerization reaction, hydrotalcite, solid base catalyst.

1. INTRODUCTION

In biorefinery process, glucose is one of the most important raw materials for producing value-added compounds and renewable liquid fuels [1-6]. Glucose is the most abundant natural monomer unit of carbohydrates, whereas fructose reveals as the most active monosaccharide for production of valuable compounds [1] such as 5-hydroxymethylfurfural (HMF) [7-9] and levulinic acid (LA) [10-12]. It is well known that the dehydration of aldohexose sugar (glucose) to HMF or LA is much more difficult than ketohexose sugar (fructose) [1], and consequently, the direct transformation of glucose to value-added compounds is not as efficient and selective as from fructose. Therefore, the transformation of glucose to fructose plays a key step for manufacturing renewable chemicals from biomass resource.

Traditionally, glucose-fructose isomerization is catalyzed by enzymes because of their excellent conversion and selectivity. However, enzymes face high price and require strict reaction conditions such as temperature, pH, as well as refined raw materials [13-14]. Other homogeneous catalysts like NaOH,

[Al(OH)₄], *etc.* possess high activity, but cause severe troubles such as recovery, reuse, environmental pollution, and corrosion of equipment [15, 16]. Moreover, the monosaccharides are unstable under strong basic medium [17]. These stimulate to search for heterogeneous catalysts to replace homogeneous catalysts for isomerization of glucose to fructose. Hydrotalcites (HTs) or hydrotalcite-like compounds are considered as the potential heterogeneous catalyst candidates. HTs or HT-like compounds can act as solid base catalysts that are widely utilized for various reactions [18-20].

In this study, we announce the fabrication of solid base catalysts based on Mg-Al hydrotalcites compounds and study on the glucose-fructose isomerization over prepared HTs in water medium.

2. EXPERIMENTAL

2.1. Materials

Al(NO₃)₃·9H₂O, Mg(NO₃)₂·6H₂O, Na₂CO₃, NaOH were provided by Xilong Chemical Co., Ltd. glucose and fructose were purchased from Sigma-Aldrich Co., and distilled water.

2.2. Fabrication of Mg-Al hydrotalcites and characterization techniques

HTs were fabricated by constant pH at low supersaturation method that was reported in our previous research [21]. Typically, solutions A and B were slowly added simultaneously at flow rate of 1 mL.min⁻¹ into a 250-mL round-bottom flask containing 50 mL of water and vigorously stirred by a magnetic stirrer at room temperature. The A solution was x moles of Mg(NO₃)₂ in 100 mL of water, and the B solution consisted of y and 0.01 moles of NaOH and Na₂CO₃ in 100 mL of water, respectively. The x and y values were varied versus expected molar ratio of Mg/Al. The obtained mixture was heated in an oil-bath at 65 °C for 12 h. After aging period, the solid was recovered by filtration and intensively washed by 2 L of water until pH of filtrate reached *ca.* 7. Finally, product (HT) was dried at 80 °C for 24 h followed by a grind to fine powder. Solids were fabricated with Mg/Al molar ratios from 1 to 5 denoted as HT1-HT5, respectively.

The phase composition and crystal structure of HTs were analyzed by X-Ray Diffraction method. XRD data were collected from D8 AVANCE Bruker diffractometer using the CuK_α radiation, $\lambda = 0.15406$ nm with an X-ray generator working at 40 kV and 40 mA.

2.3. Procedure of glucose-fructose transformation

The activity of HT was tested on the isomerization of glucose to fructose. Briefly, 0.3 g of glucose, 0.3 g of HT and 3 mL of water were introduced into 10-mL glass reactor. The reactor was closed by a teflon and silicone-lined plastic cap, then heated in an oil-bath at different temperatures. After expected time, the reactor was taken out and dipped immediately in cool water in order to quench the reaction. Reaction mixture was diluted 5 times followed by filtration through 2- μ m Millipore filter unit before HPLC analysis to determine the contents of glucose and fructose.

The reactant and product amounts were determined by a high performance liquid chromatograph (Agilent 1100) equipped with SupelcospilTM LC-NH₂ column (Agilent) and a refractive index detector. The conditions for the analysis were set as follows: acetone/water (7:3 in volume) eluent at flow rate of 1 mL.min⁻¹, both of column and detector were operated at 35 °C. Typically, the retention times of glucose and fructose were 6.81 and 7.55 min, respectively.

The conversion (Conv.) of reactant, yield and

selectivity (Sel.) of product were calculated by following formulas:

$$\text{Conv. (\%)} = \frac{\text{reacted moles of reactant}}{\text{initial moles of reactant}}$$

$$\text{Yield (\%)} = \frac{\text{obtained moles of product}}{\text{initial moles of reactant}}$$

$$\text{Sel. (\%)} = \frac{\text{obtained moles of product}}{\text{reacted moles of reactant}}$$

3. RESULTS AND DISCUSSION

All samples were inspected by X-ray diffraction. The XRD patterns of HTs exhibit 7 distinguishable diffraction peaks observed at 2θ of 11.2°, 22.6°, 34.4°, 38.5°, 45.5°, 60.3° and 61.8°. These peaks are assigned to (003), (006), (009), (015), (018), (110) and (113) planes which are the characteristics of hexagonal crystal system with space group of $R3m$ (JCPDS 22-0700). There are no any foreign peaks belonging to contaminations. It demonstrates the single phase of all fabricated samples.

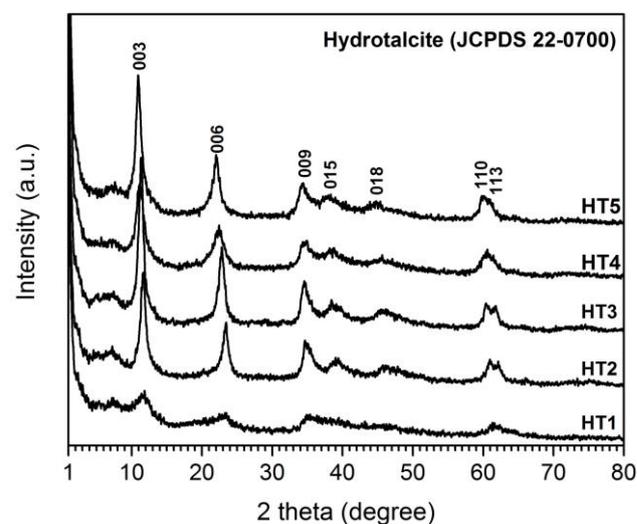


Figure 1: XRD patterns of hydrotalcites with different Mg/Al molar ratios

XRD pattern of HT1 sample had low intensity peaks indicating the most amorphous nature of solid. The cause might be the replacement of significant amount of Mg²⁺ by Al³⁺ that could destroy structure of hydrotalcite. Therefore, following discussion should be applied from HT2 to HT5 which exhibited better crystallinity.

As shown in the previous study [21], the interlayer spacing u of brucite-like layers in HTs could be derived from d -spacing of 003 planes and lattice parameter c of hexagonal unit cell. The result revealed that when Mg/Al molar ratio increased from HT2 to HT5, the c parameter, as well as

interlayer spacing u also gradually increased. That change could be explained by the substitution of small cations Al^{3+} (radius of 68 pm) by larger cations Mg^{2+} (radius of 86 pm) in octahedra causing the expansion of HT unit cell, consequently, making the increase in interlayer spacing u . The change in the interstice u will affect significantly the catalytic activities of HTs, *vide infra*.

Catalytic activities of HTs were examined in the transformation of glucose to fructose. The HPLC standard lines for glucose and fructose were constructed in concentration range of 1-25 mg/mL. The linear regression equations for glucose and fructose are $y = 1.3316x + 0.5296$ ($R^2 = 0.9992$) and $y = 1.6828x + 0.6911$ ($R^2 = 0.9998$), respectively, in which, in which y represents for content of glucose or fructose, while x is HPLC peak area.

Table 1: HPLC analysis results and calculated catalytic activities of various solid base catalysts

Catal.	HPLC peak area ($\times 10^5$)		Content (mg/mL)		Conv. (%)	Yield (%)	Sel. (%)
	Glu.	Fruc.	Glu.	Fruc.			
HT1	24.58	3.18	18.05	1.48	9.7	7.4	76.1
HT2	22.00	4.80	16.12	2.44	19.4	12.2	62.9
HT3	20.77	5.00	15.19	2.56	24.0	12.8	53.3
HT4	20.28	5.06	14.83	2.60	25.9	13.0	50.3
HT5	18.78	6.18	13.70	3.26	31.5	16.3	51.8
$Mg(OH)_2$	18.27	5.77	13.32	3.02	33.4	15.1	45.2
$Al(OH)_3$	22.48	1.94	16.48	0.74	17.6	3.7	21.1
Blank	27.04	0.00	19.91	0.00	0.5	0.0	0.0

Reaction conditions: glucose (0.3 g), catalyst (0.3 g), water (3 mL), reaction temperature (120 °C), reaction time (20 min).

Various solid bases comprising HT1-HT5 and two references $Mg(OH)_2$ and $Al(OH)_3$ were used as catalysts for isomerization. In the absence of catalyst, only 0.5 % glucose disappeared by slow decomposition without product at all. $Mg(OH)_2$ promoted the formation of 15.1 % fructose yield that was slightly smaller than HT5 (16.3 %), while $Al(OH)_3$ gave quite low activity with fructose yield of 3.7% compared with other HTs.

Alongside HT1-HT5 chain, it is easy to recognize that the fructose yield gradually increased. That trend was direct relationship with Mg/Al molar ratio in the composition of HTs, as well as the base site density on the surface of solids (base site density was determined by previous work [18]). As mentioned in the XRD section, the increase in Mg/Al molar ratio led to the expansion of interlayer spacing u , subsequently yielding some consequences

as follows: (i) elevating the surface area; (ii) rising the ability of mass transfer of substances between reaction mixture and catalyst surface; (iii) increasing the quantity of counter-ions such as OH^- , CO_3^{2-} and HCO_3^- inside the interstices of hydroxide layers leading to the increase in base site density. All those factors stimulated the conversion of glucose into fructose. Therefore, the fructose yield increased from HT1 to HT5. The analysis results also showed that the selectivity did not achieve 100 %. In other words, a part of glucose converted to unexpected products. In addition, fructose easily decomposed in the basic medium leading to the decrease in selectivity. Consequently, from HT1 to HT5, the glucose conversion and fructose yield increased, but the selectivity gradually decreased. HT5 is the best catalyst among tested solids for transformation of glucose to fructose. HT5 was selected for further investigations.

The glucose-fructose isomerization reaction is strongly influenced by the temperature. In order to assess the effect of the temperature on the reaction performance, the reactors were heated at different temperatures in range of 80-140 °C under the catalysis of HT5.

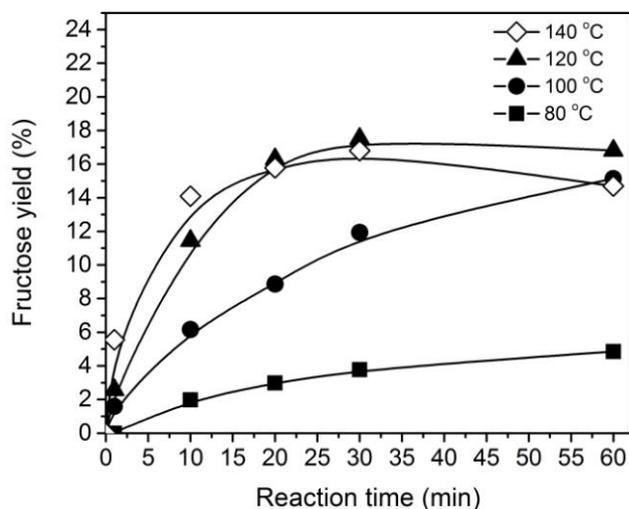


Figure 2: The time profiles of fructose yield at different reaction temperatures. Reaction conditions: glucose (0.3 g), HT5 (0.3 g), water (3 mL)

The time profile for each reaction temperature was shown in Fig. 2. The reaction took place very fast at 120 °C and 140 °C. The maximum fructose yield was reached only after 30 min of the reaction. After that, the fructose yields decreased gradually because fructose was degraded partly at high temperature as reported in references [22-24]. At temperatures below 100 °C, the reaction was much slower and needed longer time to reach the maximum fructose yield. At 120 °C the fructose

yield (17 %) and selectivity (46 %) were maximum after 20 min. When extending the reaction time longer than 20 min, the fructose yield slightly increased, but its selectivity decreased significantly. At 140 °C or higher, both fructose and glucose were strongly degraded into unexpected substances. Therefore, 120 °C and 20 min were the optimum temperature and time for isomerization of glucose by HT catalyst.

Aiming to estimate the stability and reuse of catalyst, the reaction mixtures were transferred to centrifugation tube for separating solid. The obtained solid was dried at 100 °C for 2 h and carried out XRD analysis before next reaction cycles. After each cycle, the content of glucose and fructose were analyzed by HPLC to determine the change in conversion and yield (Fig. 3).

The results indicated the gradual decrease in glucose conversion and fructose yield after 3 runs. The decline of catalytic activity after each run was blamed on the deposition of side products on the surface of solid catalyst. These contaminations might cover the catalytic sites leading the depletion of catalytic activity. The diffraction peaks of XRD pattern of recovered HT5 after the third run were slightly weaker than those of fresh one (Fig. 4e, f), however, their positions were intact without foreign peaks. It meant that the nature and phase composition of catalyst did not change after reaction cycles. The deposition of unexpected substances on solid surface might cause the decrease in XRD peaks. Nevertheless, HT5 could be recovered easily and still work several times before losing all activity.

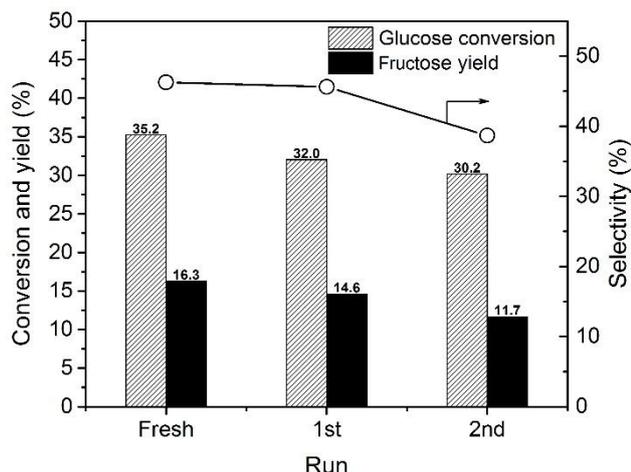


Figure 3: Recycling study of HT5 catalyst in the isomerization of glucose to fructose. Reaction conditions: glucose (0.3 g), HT5 (0.3 g), water (3 mL), reaction temperature (120 °C), reaction time (20 min)

To overcome the depletion of catalytic activity

caused by decomposition of contaminations of catalyst surface, a regeneration process is necessary. For this purpose, the catalyst after some reaction cycles was calcined at high temperature to remove contaminations completely. From thermo-analysis result from the previous work [21], at 500 °C, the mass of solid did not change anymore. Moreover, that temperature also ensured the complete decomposition of organic residue on solid catalyst. Consequently, we carried out the calcination at 500 °C. Higher temperature should not be chosen because of another reaction between MgO and Al₂O₃ to form MgAl₂O₄ spinel phase. The regeneration process comprised two steps: (i) the HT5 catalyst after 3 reaction runs was collected and calcined in air flow at 500 °C for 4 h followed by an XRD analysis, (ii) obtained solid was transferred to a reactor and reacted with 3 mL of water. An amount of 0.3 g of glucose was introduced to that reactor to test the activity of regenerated catalyst. After reaction, the catalyst was collected, dried and analyzed for the phase composition by XRD once again.

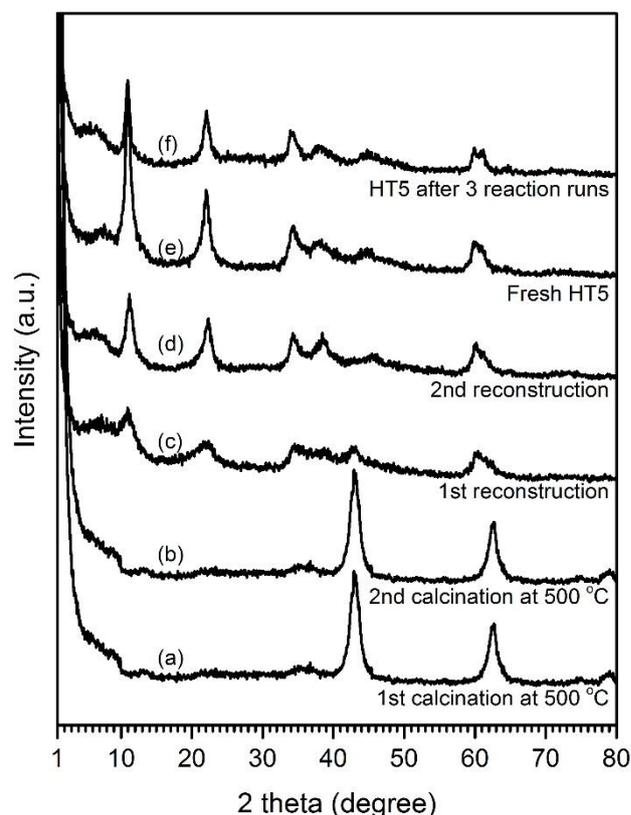


Figure 4: XRD patterns of HT catalyst after the reconstruction, calcination and recycle processes

The catalytic activity of regenerated HT5 was compared with those of fresh and 2nd-recycled HT5. It is easy to recognize that the catalytic activity of

regenerated HT5 was similar to that of fresh HT5 (16.3 % fructose yield) and was better than recycled catalyst. However, the selectivity of fructose over regenerated HT5 was lower than fresh and recycled catalysts. It meant that large amount of reactant was converted into side products.

Table 3: The catalytic activity of reconstructed HT compared with those of fresh and recycled ones

Catal.	HPLC peak area ($\times 10^5$)		Content (mg/mL)		Conv. (%)	Yield (%)	Sel. (%)
	Glu.	Fruc.	Glu.	Fruc.			
HT	18.78	6.18	13.70	3.26	31.5	16.3	51.8
HT-rec ^a	18.63	5.61	13.59	2.92	32.0	14.6	45.6
HT-reg ^b	10.58	6.19	7.54	3.27	62.3	16.3	26.2

Reaction conditions: glucose (0.3 g), catalyst (0.3 g), water (3 mL), reaction temperature (120 °C), reaction time (20 min), ^arecycled HT, ^bregenerated HT.

To elucidate the generation process, the XRD data of calcined HT5 and recovered HT5 after reaction of the 1st regeneration were collected (Fig. 4a, c). It found that at 500 °C, the phase of solid changed because of the appearance of 3 peaks at 2θ of 43.0° , 62.6° and 79.0° that were assigned to (200), (220) and (222) planes of MgO phase (JCDPS 45-0946), Fig. 4a. Therefore, after calcination at 500 °C, HT5 disassociated to MgO and Al₂O₃ (Al₂O₃ phase did not appear on XRD pattern because of its very low crystallinity). The XRD pattern of HT5 after regeneration (Fig. 4c) possessed all characteristics of hydrotalcite and was the same as fresh HT5 (Fig. 4e) although the peak intensities were lower. We can conclude that the HT5 disassociated to MgO and Al₂O₃ solids, but reconstructed to original structure of hydrotalcite after the interaction with water. The same result could be observed for the second regeneration and reconstruction (Fig. 4b, d). It can refer that hydrotalcite is a structure-memory solid base during regeneration and reconstruction processes.

In order to check the heterogeneous nature of HT-catalyzed glucose isomerization reaction, two experiments were done. In the first experiment, the catalyst was removed from reaction mixture at time of 5 min by centrifugation (6000 rpm for 5 min). The filtrate was continued to react at the same conditions to monitor the changes of glucose conversion and fructose yield. Another experiment acted as reference with the catalyst being kept in reactor the whole reaction time. The results (Fig. 5) showed that the fructose yield no longer increased

alongside the reaction time (kept almost unchanged at 5.2 %) when the catalyst was removed after 5 min. This result confirmed that the isomerization reaction catalyzed by ZrC was truly heterogeneous.

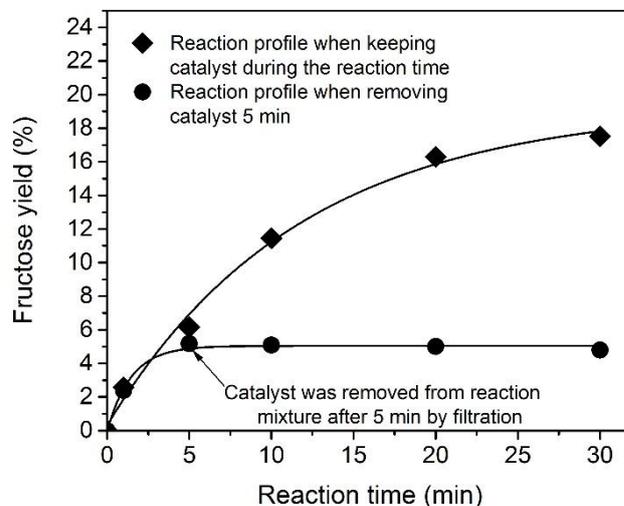


Figure 5: Experiment for checking the heterogeneous nature of HT catalyst. Reaction conditions: glucose (0.3 g), HT5 (0.3 g), water (3 mL), reaction temperature (120 °C), reaction time (1-30 min)

4. CONCLUSION

The HTs series are successfully synthesized by a constant pH at low supersaturation method. The catalytic activity of HT5 was highest (16.3 % fructose yield) among tested solid base catalysts under optimum reaction conditions (120 °C and 20 min). HT5 reveals a good reuse ability in the recycle experiments with stable structure and activity. Hydrotalcites are also a structure-memory materials during regeneration and reconstruction processes. The regeneration takes place perfectly giving phase composition and crystallinity to be the same as fresh HT, and the regeneration-reconstruction process can be repeated many times. HTs are truly heterogeneous easily separated from reaction mixture by centrifugation or filtration.

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