

PREPARATION AND CHARACTERISTICS OF SOLID BASE HYDROTALCITE

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Abstract

In this report, we announce the fabrication of hydrotalcite compounds (HTs) with different molar ratios of Mg/Al by constant pH at low supersaturation method. The obtained compounds could serve as solid base catalysts. The crystal structure and phase composition were investigated by X-Ray Diffraction technique. The increase in Mg/Al molar ratio led to the expansion of the interlayer spacings of brucite-like layers in HTs because of the substitution of small ions (Al^{3+}) by larger ions (Mg^{2+}) in the octahedra of hydroxide layers. The elemental analysis proved the compatibility of experimental Mg/Al molar ratios and theoretical values. The presence of function groups was elucidated by FT-IR method. The results of thermo-analysis exhibited that the structure of HTs collapsed at temperatures higher than 400 °C due to the dissociation of HTs to MgO and Al_2O_3 . The base site density determined by titration method was found to be directly related with Mg/Al molar ratio. The catalytic activity was tested on the glucose to fructose isomerization reaction. In all tested samples, HT5 gave the highest activity with fructose yield of 16.3%. Alongside HT1-HT5 chain, the catalytic activity increased versus Mg/Al molar ratio, as well as the density of base site.

Keywords. Hydrotalcite, solid base catalyst, glucose, fructose, isomerization reaction.

1. INTRODUCTION

The isomerization reaction of monosaccharides is a key step in the sequential reaction chain of transformation of lignocellulosic materials to value-added fuels and chemicals [1-6]. Among them, the conversion of glucose into fructose plays a very important role because 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 [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]. Therefore, the direct transformation of glucose to value-added compounds is not as efficient and selective as from fructose.

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, $[\text{Al}(\text{OH})_4]^-$, etc. possess high activity, but cause severe troubles such as recovery, reuse, environmental pollution, and corrosion of equipments [15, 16]. Moreover, the monosaccharides are unstable under strong basic medium [17]. These are driving forces to search for heterogeneous catalysts to replace homogeneous catalysts for isomerization of glucose to fructose.

In this study, we announce the fabrication of solid base catalysts based on hydrotalcite (HT) compounds that can serve as recyclable solid base catalysts for isomerizing glucose to fructose in water medium.

2. EXPERIMENTAL

2.1. Materials

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Na_2CO_3 , NaOH were provided by Xilong Chemical Co., Ltd. 36 wt% HCl, NaCl, HCOOH, glucose and fructose were purchased from Sigma-Aldrich Co., and

distilled water.

2.2. Fabrication of hydrotalcite and characterization techniques

In this research, HTs were fabricated by constant pH at low supersaturation method. 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 *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, HT2, HT3, HT4 and HT5, respectively.

The characteristics of fabricated materials were discovered by various techniques: X-Ray Diffraction (XRD) patterns were recorded on a D8 ADVANCE Bruker diffractometer using the CuK α radiation, $\lambda = 0.15406$ nm with an X-ray generator working at 40 kV and 40 mA. The data were collected with $2\theta = 5$ - 80° at scanning rate of 1° min^{-1} . Thermal analyses were carried out on a Labsys TG/DSC 1600 SETARAM system from RT to 800 °C at heating rate of $10^\circ \text{ C} \cdot \text{min}^{-1}$ in air with flow rate of $2.5 \text{ L} \cdot \text{h}^{-1}$. FT-IR spectra were recorded by an FT-IR Affinity-1S Shimadzu spectrometer. The Mg/Al molar ratios were determined by ICP method using Elan 9000 Perkin Elmer equipment. The base site content was calculated from titration result of HT with 0.0096 M HCOOH and phenolphthalein indicator.

2.3. Catalytic activity test

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- μm 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 SupelcosilTM 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

In order to determine the crystal structure, all samples were inspected by X-ray diffraction. The XRD patterns of HTs exhibited 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 were assigned to (003), (006), (009), (015), (018), (110) and (113) planes which are the characteristics of hexagonal crystal system with space group of $R\bar{3}m$ (JCPDS 22-0700). There were not any foreign peaks belonging to contaminations. It demonstrated the single phase of all fabricated samples.

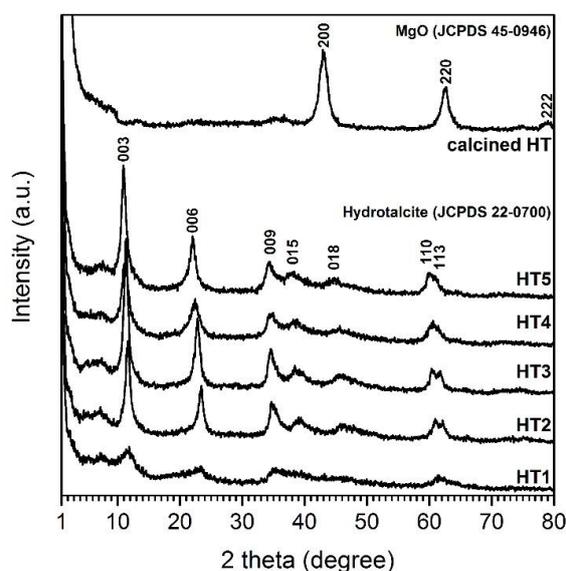


Fig. 1: XRD patterns of hydrotalcites with different Mg/Al molar ratios and a calcined sample

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 Mg^{2+} by Al^{3+} that could destroy structure of hydroxalcite. Therefore, following discussion should be applied from HT2 to HT5 which exhibited better crystallinity.

In the structure of HT, a value is also equal the cation-cation distance in the hydroxide layer and can be inferred from d_{110} by following equation:

$$a = 2 \times d_{110}$$

whereas, c parameter is given by formula:

$$c = 3 \times d_{003}$$

On the other hand, c value is sum of hydroxide layer thickness (4.9 Å) and interlayer spacing (u). Therefore, the interstice u is calculated as follows:

$$u = c - 4.9 = 3 \times d_{003} - 4.9$$

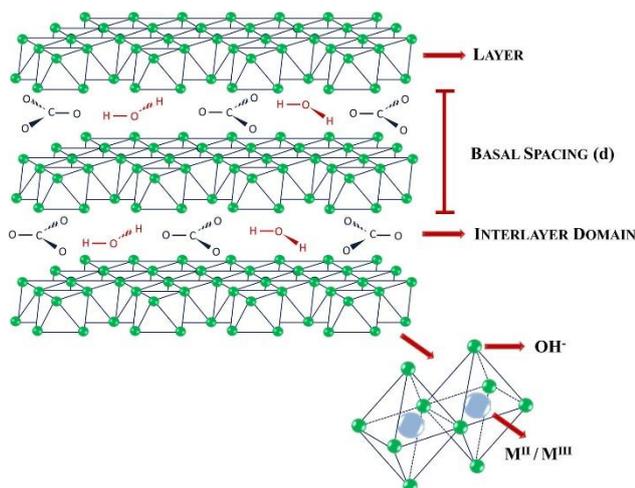


Fig. 2: Layered double hydroxide structure of hydroxalcite compound [18]

Table 1: d -spacings and lattice parameters c , u (Å) of various HT compounds

hkl	HT1	HT2	HT3	HT4	HT5
003	7.633	7.606	7.805	7.939	8.077
006	3.900	3.785	3.889	3.955	4.029
009	2.552	2.589	2.593	2.598	2.603
015	-	2.305	2.342	2.331	2.365
018	-	1.966	1.889	1.987	1.994
110	1.502	1.518	1.531	1.527	1.541
113	-	1.491	1.499	-	-
c	22.89	22.82	23.42	23.82	24.23
u	17.99	17.92	18.52	18.92	19.33

The calculated d -spacings and lattice parameters of all HT were listed in Table 1. It is easy to recognize 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 spacings u . The XRD pattern of HT sample calcined at 450 °C revealed that HT was not stable at high temperature, it decomposed to MgO (JCPDS 45-0946) and Al_2O_3 (diffraction peaks of Al_2O_3 could not appear because of amorphous state). This means that the HT structure was not stable at temperature higher than 400 °C and the detail discussion will be shown in thermo-analysis results, *vide infra*.

In order to determine the molar ratio of Mg/Al in all prepared samples, a defined amount of each solid was dissolved in dilute HCl solution. The contents of Mg^{2+} and Al^{3+} were measured by ICP-MS technique. The results were shown in Table 2.

Table 2: Metal content in solid determined by ICP-MS

Sample	Content (ppm)		Mg/Al molar ratio*	
	Mg	Al	Exp.	Theory
Blank	17.98	16.97	-	-
HT1	149.41	183.93	0.89	1
HT2	254.52	160.11	1.86	2
HT3	358.09	150.17	2.87	3
HT4	524.16	159.89	3.98	4
HT5	626.95	155.86	4.93	5

$$* \text{ Mg/Al molar ratio} = \frac{(C_{Mg} - C_{Mg}^0)/24}{(C_{Al} - C_{Al}^0)/27}$$

The experimental molar ratio of Mg/Al well agreed with theoretical values in stoichiometric formulas demonstrating that all taken quantities of metals in precursors participating the structure of HTs.

The thermo-gravimetric curve showed two stages of mass loss associating two endothermic effects at *ca.* 180 °C and 400 °C. The first mass loss of 12.20% at low temperature was attributed to the loss of interlayer waters, without collapse of the structure, this step was reversible. The second one (31.38%) at higher temperature was due to the loss of hydroxyl groups from brucite-like layer, as well as the anions (CO_3^{2-}). After the second mass loss, the structure of HT was destroyed completely, XRD study exhibited the disappearance of HT phase and

the appearance of new phases MgO and Al₂O₃ in thermo-treated HT solids.

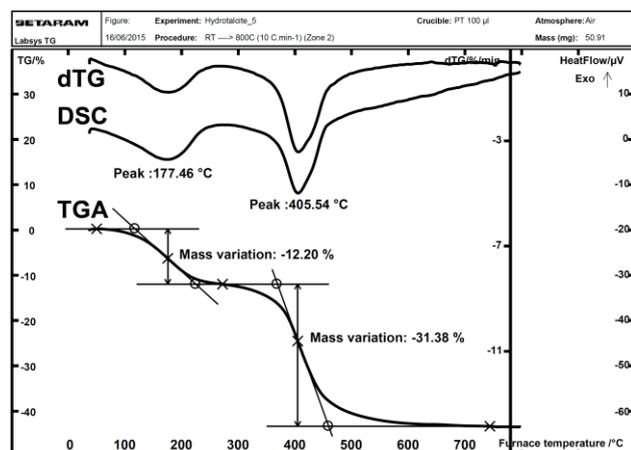


Fig. 3: TG/DSC curves of a hydrotalcite sample

The absorption at 3500-3650 cm⁻¹, present in all HTs, was attributed to the H-bonding stretching vibrations of the OH group in the brucite-like layer. The absorption band at 3000 cm⁻¹ belonged to hydrogen bonding between H₂O and the anions in the interlayer. An H₂O bending vibration also occurred at 1650 cm⁻¹. The bands at 1360 and 620 cm⁻¹ were assigned to asymmetric stretching and bending vibration modes in CO₃²⁻ anions. The absorption bands at 920, 560 and 460 cm⁻¹ were assigned to stretching vibration of Al-OH groups, stretching vibration of Mg-OH groups affected by Al³⁺ cations, and stretching vibration mode of Mg-OH groups, respectively.

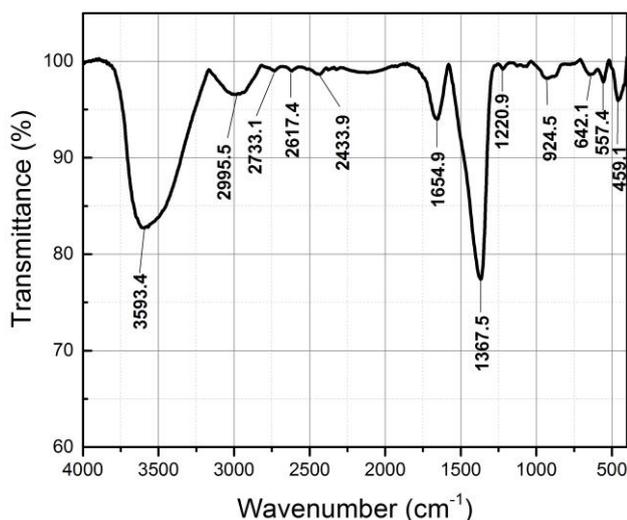


Fig. 4: IR spectrum of hydrotalcite

The standard formic acid (FA) solution with concentration of 0.0096 M was utilized to titrate the base sites of HTs. The HT was stirred with 10 wt%

NaCl solution before titration. NaCl served as ion-exchange agent to release the base sites from the solids. Assuming that each base site bound only one molecule of formic acid, the base site density was given by below formula and listed in Table 3.

$$\text{Base site density} = \frac{\bar{V}_{\text{FA}} \times C_{\text{FA}}}{m} \text{ (mmol.g}^{-1}\text{)}$$

In which C_{FA} , V_{FA} are concentration and consumed volume of formic acid, m is taken weight of hydrotalcite for titration.

Alongside HT1-HT5 chain, the base site density increased gradually. This phenomenon was elucidated by the increase in interlayer spacing versus the Mg/Al molar ratio of HTs that was exposed by XRD discussion above. The expansion of those interstices might elevate the quantity of small molecules that served as base sites such as OH⁻, HCO₃⁻, CO₃²⁻, and so on.

Table 3: Titration result and base site density in HTs

Sample	V _{FA} (mL)			Base site density (mmol.g ⁻¹)
	1 st run	2 nd run	3 rd run	
HT1	11.2	11.1	11.0	1.07
HT2	12.5	12.7	12.5	1.21
HT3	13.5	13.5	13.6	1.30
HT4	17.2	17.5	17.5	1.67
HT5	19.0	20.0	18.8	1.85

Conditions: 0.0096 M FA, $m = 0.1$, H₂O (2 mL), NaCl (0.37 g), phenolphthalein indicator.

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 were $y = 1.3316x + 0.5296$ ($R^2 = 0.9992$) and $y = 1.6828x + 0.6911$ ($R^2 = 0.9998$), respectively. Various solid base 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.

Table 4: 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).

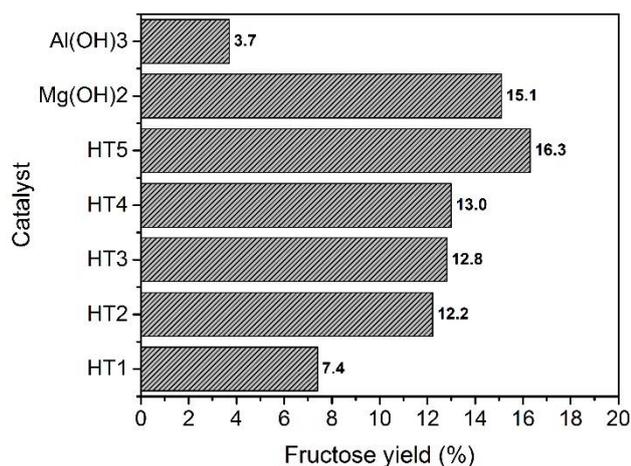


Fig. 5: The dependence of obtained fructose yield on different solid base catalysts

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⁻, CO₃²⁻ and HCO₃⁻ 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.

4. CONCLUSION

HTs were successfully fabricated by constant pH at low supersaturation method. All obtained HTs had single phase that belonged to hexagonal crystal system. The increase in Mg/Al molar ratio led to the expansion of interlayer spacings yielding the gain of base site density. The base site density was determined from titration method showing the rise of base site amount versus Mg/Al molar ratio. Element analysis exhibited the good agreement between experimental molar ratio of Mg/Al and expected ratio in all samples from HT1 to HT5. The presence of function groups (OH⁻, CO₃²⁻, metal-oxygen bonds) were proved by FT-IR method. The HTs were not stable above 450 °C because of decomposition to MgO and Al₂O₃ phases. All prepared samples could expose the activity as solid base catalysts for glucose-fructose isomerization, in which HT5 gave highest fructose yield (ca. 16.3%). The increase in Mg/Al molar ratio led to the expansion of interstices of hydroxide layers in HTs, as well as the rise of base site content, and subsequently, the increase in the fructose yield.

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REFERENCES

1. A. Corma, S. Iborra and A. Velty. *Chemical Routes for the Transformation of Biomass into Chemicals*, Chem. Rev., **107**, 2411-2502 (2007).
2. M. E. Zakrzewska, E. Bogel-Lukasik and R. Bogel-Lukasik. *Ionic Liquid mediated Formation of 5-Hydroxymethylfurfural - A Promising Biomass-derived Building Block*, Chem. Rev., **111**, 397-417 (2011).
3. J. C. Escobar, E. S. Lora, O. J. Venturini, E. E. Yanez, E. F. Castillo and O. Almazan. *Biofuels: Environment, Technology and Food Security*, Renew. Sustain. Energy Rev., **13**, 1275-1287 (2009).
4. J. P. M. Sanders, J. H. Clark, G. J. Harmsen, H. J. Heeres, J. J. Heijnen, S. R. A. Kersten, W. P. M. van Swaaij and J. A. Moulijn. *Process Intensification in the Future Production of Base Chemicals from Biomass*, Chem. Eng. Process., **51**, 117-136 (2012).
5. X. Tong, Y. Ma and Y. Li. *Biomass into Chemicals: Conversion of Sugars to Furan Derivatives by*

- Catalytic Processes*, Appl. Catal. A: Gen, **385**, 1-13 (2010).
6. J. C. Serrano-Ruiz, A. Pineda, A. M. Balu, R. Luque, J. M. Campelo, A. A. Romero and J. M. Ramos-Fernandez. *Catalytic Transformations of Biomass-derived Acids into Advanced Biofuels*, Catal. Today, **195**, 162-168 (2012).
 7. A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani. *A One-pot Reaction for Biorefinery: Combination of Solid Acid and Base Catalysts for Direct Production of 5-Hydroxymethylfurfural from Saccharides*, Chem. Commun., 6276-6278 (2009).
 8. M. Ohara, A. Takagaki, S. Nishimura and K. Ebitani. *Syntheses of 5-Hydroxymethylfurfural and Levoglucosan by Selective Dehydration of Glucose Using Solid Acid and Base Catalysts*, Appl. Catal. A: Gen., **383**, 149-155 (2010).
 9. Kl. Beckerle and J. Okuda. *Conversion of Glucose and Cellobiose into 5-Hydroxymethylfurfural (HMF) by Rare Earth Metal Salts in N,N-dimethylacetamide (DMA)*, J. Mol. Catal. A: Chem., **356**, 158-164 (2012).
 10. J. Jow, G. L. Rorrer and M. C. Hawley. *Dehydration of D-fructose to Levulinic Acid over LZV Zeolite Catalyst*, Biomass, **14**, 185-194 (1987).
 11. W. Zeng, D. G. Cheng, H. Zhang, F. Chen and X. Zhan. *Dehydration of Glucose to Levulinic Acid over MFI-type Zeolite in Subcritical Water at Moderate Conditions*, Reac. Kinet., Mech. Catal., **100**, 377-384 (2010).
 12. P. A. Son, S. Nishimura and K. Ebitani. *Synthesis of Levulinic Acid from Fructose using Amberlyst-15 as a Solid Acid Catalyst*, Reac. Kinet., Mech. Catal., **106**, 185-192 (2012).
 13. S. H. Bhosale, M. B. Rao and V. V. Deshpande. *Molecular and Industrial Aspects of Glucose Isomerase*, Microbio. Rev., 280-300 (1996).
 14. Y. Zhang, K. Hidajat and A. K. Ray. *Optimal Design and Operation of SMB Bioreactor: Production of High Fructose Syrup by Isomerization of Glucose*, Biochem. Eng. J., **21**, 111-121 (2004).
 15. C. Kooyman, K. Vellenga and H. G. J. De Wilt. *The Isomerization of D-glucose into D-fructose in Aqueous Alkaline Solutions*, Carbohydr. Res., **54**, 33-44 (1977).
 16. M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura and H. Inomata. *Catalytic Glucose and Fructose Conversions with TiO₂ and ZrO₂ in Water at 473 K: Relationship between Reactivity and Acid-Base Property Determined by TPD Measurement*, Appl. Catal. A: Gen., **295**, 150-156 (2005).
 17. B. Y. Yang and R. Montgomery. *Alkaline Degradation of Glucose: Effect of Initial Concentration of Reactants*, Carbohydr. Res., **280**, 27-45 (1996).
 18. D. G. Evans and R. C. T. Slade. *Structural aspects of layered double hydroxides*, Springer (p 1-87), New York (2006).

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