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Mizuho Yabushita

A Study on Catalytic Conversion of Non-Food Biomass into Chemicals

Fusion of Chemical Sciences and Engineering

Doctoral Thesis accepted by
Hokkaido University, Sapporo, Japan

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2. Yabushita M, Kobayashi H, Fukuoka A (2014) Catalytic transformation of cellulose into platform chemicals. Appl Catal B Environ 145:1–9
3. Yabushita M, Kobayashi H, Hasegawa J, Hara K, Fukuoka A (2014) Entropically Favored Adsorption of Cellulosic Molecules onto Carbon Materials through Hydrophobic Functionalities. ChemSusChem 7(5):1443–1450
4. Yabushita M, Kobayashi H, Hara K, Fukuoka A (2014) Quantitative evaluation of ball-milling effect on hydrolysis of cellulose catalysed by activated carbons. Catal Sci Technol 4(8):2312–2317
5. Yabushita M, Kobayashi H, Shrotri A, Hara K, Ito S, Fukuoka A (2015) Sulfuric Acid-Catalyzed Dehydration of Sorbitol: Mechanistic Study on Preferential Formation of 1,4-Sorbitan. Bull Chem Soc Jpn 88(7):996–1002
6. Kobayashi H, Yabushita M, Hasegawa J, Fukuoka A (2015) Synergy of Vicinal Oxygenated Groups of Catalysts for Hydrolysis of Cellulosic Molecules. J Phys Chem C 119(36):20993–20999
7. Yabushita M, Kobayashi H, Kuroki K, Ito S, Fukuoka A (2015) Catalytic Depolymerization of Chitin with Retention of *N*-Acetyl Group. ChemSusChem 8(22):3760–3763
8. Kobayashi H, Yabushita M, Fukuoka A (2016) Depolymerization of Cellulosic Biomass Catalyzed by Activated Carbons. In: Schlaf M, Zhang ZC (eds) Reaction Pathways and Mechanisms in Thermocatalytic Biomass Conversion I: Cellulose Structure, Depolymerization and Conversion by Heterogeneous Catalysts. Springer Singapore, Singapore, pp 15–26

Supervisor's Foreword

Reduction of greenhouse gas emissions is a current global issue. To solve this problem, considerable attention has been focused on a biorefinery that can produce fuels and chemicals from renewable biomass. One of the key issues in that biorefinery is the utilization of non-food biomass, and lignocellulose is the most abundant non-food biomass on earth. However, the production of fuels and chemicals from lignocellulose has been a challenge owing to its recalcitrant structures consisting of cellulose, hemicellulose, and lignin. A similar situation can be seen for marine biomass; chitin is the most abundant marine biomass, but the selective conversion of chitin into chemicals has been a target. Enzymes and chemical catalysts have been used for the depolymerization of lignocellulose and chitin into monomers of their components, but known processes have difficulties in terms of cost, activity, separation, and durability of the enzymes and catalysts.

In this thesis, Dr. Mizuho Yabushita studied the conversion of non-food biomass into platform chemicals, mainly by solid catalysts. First, he focused on the hydrolysis of cellulose and succeeded in high-yield synthesis of glucose by weakly acidic carbon catalysts. Then he attained the production of glucose and xylose from bagasse pulp as a real biomass using carbon catalysts. Mix-milling of biomass substrates and solid catalysts greatly promotes the hydrolysis of polysaccharides. Also very important is his detailed study of the mechanism for hydrolysis of cellulose. He found that larger sugar molecules are favorably adsorbed on the carbon surface via hydrophobic interactions, and then the adsorbed molecules are hydrolyzed by the weakly acidic sites on the carbon. This mechanism resembles that of enzymes, but he showed the advantage of solid carbon catalysts that can work under a wide range of reaction conditions. Reduction of glucose gives sorbitol, and Dr. Yabushita realized the selective dehydration of sorbitol to 1,4-sorbitan as a valuable compound. He also achieved the catalytic depolymerization of chitin to monomers with retention of *N*-acetyl groups.

His findings will contribute to establishing new processes of catalytic conversion of non-food biomass in biorefineries and, moreover, to implementing a sustainable society in the future.

Sapporo, Japan
November 2015

Prof. Atsushi Fukuoka

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Berkeley, USA
October 2015

Mizuho Yabushita

Contents

Abbreviations

3A5AF	3-Acetamido-5-acetylfuran
3-HPA	3-Hydroxypropionic acid
5-HMF	5-Hydroxymethylfurfural
AC	Activated carbon
ACC	Aqueous counter collision
ADP	Adenosine diphosphate
AFEX	Ammonia fiber explosion
AH1	Unidentified mono-anhydrohexitol 1
AH2	Unidentified mono-anhydrohexitol 2
APCI	Atmospheric pressure chemical ionization
ATP	Adenosine triphosphate
B3LYP	Becke 3-parameter Lee-Yang-Parr
BET	Brunauer-Emmett-Teller
[BMIM]Cl	1-Butyl-3-methylimidazolium chloride
CBH	Cellobiohydrolase
CNF	Carbon nanofiber
CNT	Carbon nanotube
CP/MAS	Cross polarization/magic angle spinning
CP-SO_3H	Sulfonic chloromethyl polystyrene resin
CrI	Crystallinity index
CVD	Chemical vapor deposition
DEPT	Distortionless enhancement by polarization transfer
DF	Degree of freedom
DFT	Density functional theory
DMAc	*N*,*N*-Dimethylacetamide
DMF	2,5-Dimethylfuran
DMSO	Dimethyl sulfoxide
DOE	Department of Energy
DP	Degree of polymerization
DRIFT	Diffuse reflectance infrared Fourier transform
DTGS	Deuterated triglycine sulfate

EDX	Energy dispersive X-ray spectroscopy
EG	Endoglucanase
FDCA	2,5-Furandicarboxylic acid
GC	Gas chromatography
GlcN	Glucosamine
GlcNAc	*N*-Acetylglucosamine
GO	Graphene oxide
HAADP	1-*O*-(2-Hydroxyethyl)-2-acetamido-2-deoxyglucopyranoside
HADP	1-*O*-(2-Hydroxyethyl)-2-amino-2-deoxyglucopyranoside
HMBC	Heteronuclear multiple bond correlation
HMQC	Heteronuclear multiple quantum coherence
HPA	Heteropoly acid
HPLC	High-performance liquid chromatography
ICIS	International Chemical Information Service
ICP-AES	Inductivity coupled plasma atomic emission spectroscopy
IL	Ionic liquid
IR	Infrared
LC/MS	Liquid chromatography/mass spectroscopy
MC	Mesoporous carbon
MCT	Mercury-cadmium-telluride
MeGlc	1-*O*-Methylglucose
MeGlcNAc	1-*O*-Methyl-*N*-acetylglucosamine
NAD^+	Nicotinamide adenine dinucleotide
NADH	Reduced form of nicotinamide adenine dinucleotide
NLDFT	Nonlocal density functional theory
NMR	Nuclear magnetic resonance
NREL	National Renewable Energy Laboratory
OFG	Oxygenated functional group
P(3HB)	Poly(3-hydroxybutyrate)
P(3HB-*co*-3HV)	Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)
PEIT	Polyethylene isosorbide terephthalate
PET	Polyethylene terephthalate
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene difluoride
RI	Refractive index
S/C	Substrate/catalyst
SCRF	Self-consistent reaction field
SEM	Scanning electron microscope
SZ	Sulfated zirconia
TEM	Transmission electron microscope
TEOS	Tetraethyl orthosilicate
TOC	Total organic carbon
TOF	Turnover frequency
TON	Turnover number
TOSS	Total suppression of sidebands

UV	Ultraviolet
XAFS	X-ray absorption fine structure
XRD	X-ray diffraction
YAG	Yttrium–aluminum–garnet
ZTC	Zeolite-templated carbon