Recent Developments in the Catalytic Conversion of Cellulose into Valuable Chemicals

Pengfei YANG, Hirokazu KOBAYASHI, Atsushi FUKUOKA*

Catalysis Research Center, Hokkaido University, Kita 21, Nishi 10, Kita-ku, Sapporo 001-0021, Hokkaido, Japan

Abstract: Currently, under huge pressure from energy demands and environmental problems, much attention is being paid to biomass conversion, which will play an important role in meeting the requirements for a sustainable society. As the most abundant biomass on earth, cellulose is usually used as the first research target for biomass conversion. In this review, the recalcitrant structure of cellulose is discussed and non-catalytic hydrolysis by hot-compressed water and catalytic hydrolysis using solid acids are then considered. We also review the catalytic conversion of cellulose into valuable chemicals including hexitols (sorbitol and mannitol), ethylene glycol, and related compounds using various heterogeneous catalysts.

Key words: biomass; cellulose; heterogeneous catalyst; glucose; sorbitol; hot-compressed water; hydrolysis; hydrogenation

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*Corresponding author: Tel: +81-11-706-9140; Fax: +81-11-706-9139; E-mail: fukuoka@cat.hokudai.ac.jp

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Currently, much attention is being paid to the foreseeable depletion of fossil carbon resources like crude oil, coal, and natural gas in the near future and the resultant global energy crisis. Securing the energy demand of the world by finding substitutes is a common issue for all humanity. On the other hand, the large amount of released green-house gases such as CO₂ by the consumption of fossil fuels in various industrial processes and in daily life has led to global climate change and frequent disasters occurring in the world. Controlling the emission of these gases is another urgent issue for all of us.

Biomass, photosynthesized from CO₂ and H₂O and its storage of solar energy in the form of various polymerized organic compounds is characterized by its abundance, renewability and CO₂ neutrality, and it has great potential to solve the two aforementioned issues (Fig. 1). Therefore, it is very promising as a substitute for the diminishing fossil fuel reservoirs for a sustainable society [1–3].

According to human digestion, biomass can be divided into two types: edible and inedible biomass. Edible biomass includes crops, vegetables, and fruits and these have been industrially transformed into first generation biofuels (bio-ethanol, biodiesel) with the evident drawback of competing with the production of foods and animal feed. Inedible lignocellulosic biomass is very suitable as a new energy source for the development of second generation biofuels, and this is still in its infancy [4]. Among the three major components

(cellulose, hemicellulose, and lignin) in lignocelluloses, cellulose with a content of 40%–50% is known to be the most abundant organic compound in nature [5]. It has been estimated that 10¹¹–10¹² tons of cellulose are photosynthesized annually, which is mostly combined with hemicellulose and lignin in the cell wall of woody biomass. Therefore, the conversion of cellulose by catalysis plays a principal role in the production of a variety of valuable chemicals such as glucose, sorbitol, and HMF for further bio-refinery procedures. Mineral acids or enzymes have been used as catalysts for the hydrolysis of cellulose, even under mild conditions. However, these mineral acids are environmentally unfriendly because of their corrosive property and their difficult separation from products. Additionally, high prices and unsuccessful recovery methods after the reaction limit

Fig. 1. Concept of a bio-refinery.

the application of enzymatic systems. Based on these facts, heterogeneous catalysis for cellulose conversion has attracted much attention recently. Several related reviews that highlight this area are recommended as an introduction [6–8]. In this review, we describe the recent development of cellulose conversion into valuable platform compounds using heterogeneous catalysis. Although new media like ionic liquids appear fascinating in the field of cellulose conversion because of their unique ability to dissolve recalcitrant cellulose [9], we focus on topics related to hot-compressed water (HCW), which is the most frequently used medium for the catalytic conversion of cellulose at present. Before a discussion of research development, the structural and crystalline properties of cellulose are introduced as a basis to understand its reactivity in actual studies.

1 Structures and properties of cellulose

Cellulose is a polydisperse linear homopolymer consisting of regio- and stereo-selectively β -1,4-glycosidic linked D-glucopyranose units (so-called anhydroglucose units, AGUs, Fig. 2). Unlike the α -1,4-glycosidic bonding present in starch, β -linkages between the equatorial hydroxyl groups on the C1 and C4 carbon atoms in cellulose lead to a straight chain polymer with no coils or branches and these molecules adopt an extended and rather stiff rod-like conformation [10]. It is noteworthy that the hydroxyl groups at the C2, C3, and C6 atoms of the glucose ring in one chain can form hydrogen bonds with oxygen atoms on the same or on a neighboring chain (Fig. 2), and this holds the chains firmly together side-by-side and form microfibrils with high tensile strength. The existence of the hierarchic networks of intra- and inter-molecular hydrogen bonds results in cellulose having stronger chemical recalcitrance than starch in hot water and common organic solvents such as ethanol and acetone. Concentrated acid solutions, concentrated aqueous solutions of zinc chloride, ammoniacal copper hydroxide, and ionic liquids are exceptions, however.

Cellulose exists in several crystal polymorphs, differing in unit cell dimensions and possibly in chain polarity [6,8]. The natural cellulose I has two different structures, I_α and I_β .

Cellulose produced by bacteria and algae is rich in I_α while cellulose from higher plants consists mainly of I_β . Besides cellulose I, cellulose II is another important crystalline form of cellulose. The process of the transformation of cellulose I to cellulose II is generally considered to be irreversible suggesting that cellulose II is more stable than cellulose I. With various chemical treatments it is possible to produce cellulose III and cellulose IV.

Cellulose consists of the main ordered crystalline part and a significant amorphous part [11] between which structural differences exist largely in the chain length and hydrogen bonding patterns [12]. A parameter termed the crystallinity index (CrI) has been used to describe the relative amount of crystalline cellulose. Crystalline cellulose consists of well-packed long chains, side by side, by strong hydrogen bonds and this contributes much to the aforementioned recalcitrance of cellulose. Amorphous cellulose has a length of rigid chain segments as short as the order of one cellobiose unit with a distinct characteristic that small molecules such as water can penetrate this region easily and access to the inner cellulose molecules. It is thus expected that the amorphous portion in microcrystalline cellulose is much more chemically reactive than the crystalline part, e.g. with respect to hydrolysis in HCW [13] and its hydrogenation to sugar alcohols. Obviously, an increase in the amorphous portion in cellulose helps enhance the overall reactivity of cellulose. Numerous pretreatment procedures have been developed to loosen the cellulose structure to increase the amorphous part of cellulose. These methods are divided into two categories: physical (milling, grinding, steaming, and irradiation) and chemical (dissolution, alkali, acid, swelling, gas, oxidation, and solvent) [6].

2 Hydrolysis of cellulose

Hydrolytic cleavage of the β -1,4-glycosidic bonds between the two AGUs in cellulose fibers is of fundamental interest and plays an essential role in cellulose processing, as this degradation step paves the way for other catalytic transformations [8]. Furthermore, whereas cellulose is inert to water under mild conditions it can hydrolyze at elevated

Fig. 2. Inter- and intra-molecular hydrogen bonds in the cellulose structure.

temperatures, especially in HCW where many one-pot reactions for cellulose conversion have been carried out including hydrolysis with solid acid catalysts and hydrogenation or hydrogenolysis with supported metal catalysts. Therefore, it is imperative to first highlight the area of cellulose hydrolysis in HCW media. We then discuss the hydrolysis with solid acids, especially sulfonated carbon.

2.1 Hydrolysis of cellulose in HCW

HCW is generally described as water at temperatures above 150 °C and various self-generated pressures [14]. In comparison to ambient water, HCW has a lower dielectric constant, fewer and weaker hydrogen bonds and a higher isothermal compressibility [15]. Furthermore, the solubility of most gases in liquid water initially decreases as the temperature increases above ambient but after reaching its minimum the gas solubility increases. This phenomenon is likely favorable for the diffusion of reagent gases such as O₂ or H₂ from the gaseous phase to the solid catalyst surface through HCW and as a result the catalytic activity for cellulose oxidation or hydrogenolysis reactions is promoted. Thirdly, the ionic product (K_w) for water near the critical temperature (~250 °C) is about 3 orders of magnitude higher than that of ambient water [15]. The concentrations of H⁺ and OH⁻ and their affinities are higher in HCW, rendering HCW an effective medium for acid- and base-catalyzed reactions.

As far as cellulose conversion is concerned, water molecules in HCW can hydrolyze cellulose into oligosaccharides or glucose monomers [13,16]. When comparing the hydrolysis behavior between amorphous and crystalline in microcrystalline cellulose, Yu et al. [13] found that from around 150 °C the glycosidic bonds in the amorphous part started to hydrolyze into glucose monomers while for the crystalline portion hydrolyzes at about 180 °C, and this is a result of the structural differences between amorphous and crystalline cellulose. Contrasting with the easy penetration of water molecules through the loose structure of amorphous cellulose, the hinged hydrogen bonds in the crystalline part must first be overcome so that water molecules can reach the glycosidic bonds for the hydrolysis step. The excessive energy required for the hydrolysis of the crystalline part comes from the hydrogen bonding network in crystal-

line cellulose.

The hydrolysis of cellulose in pure water, however, is definitely not catalytic because one H₂O molecule is totally consumed when breaking down the glycosidic bond in cellulose. Under an atmosphere of H₂ or O₂ together with metal catalysts the non-catalytic hydrolysis of cellulose in hot water is evidently helpful for further catalytic hydrogenation, hydrogenolysis or oxidation to produce numerous valuable chemicals. A dispute exists about whether proton species are produced from H₂ or water [6,17–20] and many studies have taken for granted that hydrolysis in HCW is a necessary initial step for further reaction steps in cellulose conversion [21–24]. On the other hand, the hydrolysis of cellulose can be improved by consecutive hydrogenation to yield useful products and prevent side reactions that give undesired by-products [17,21,24].

2.2 Catalytic hydrolysis of cellulose using solid acid catalysts

Although mineral liquid acids are highly active even under mild conditions for many acid-catalyzed reactions including the hydrolysis of cellulose, their fatal problem is the difficulty in recycling the acids and the consequent costly post-treatments such as neutralization and effluent processing, which is environmentally unfriendly. Therefore, highly active and stable solid acid catalysts are very fascinating for numerous “green” chemical processes. Hara et al. [25–28] recently developed a type of carbon-based solid acid with a high density of Brönsted acid sites (SO₃H and COOH) to pyrolytically carbonize sugars such as glucose, sucrose, or cellulose and subsequently sulfonate the as-prepared carbons (Fig. 3). It is interesting that these sulfonated carbon materials are very active for the hydrolysis of microcrystalline cellulose to produce water-soluble saccharides even at a low reaction temperature (100 °C), and conventional strong solid Brönsted acid catalysts such as niobic acid, H-mordenite, Nafion, and Amberlyst-15 had no activity [26]. The specific surface area of the sulfonated carbon was only around 2 m²/g but the yield of soluble saccharides reached nearly 70% (glucose 4%, β-1,4-glucan 64%). Their catalytic performance was attributed to their intrinsic ability to adsorb β-1,4-glucan, which is not adsorbed on the other solid acids. Furthermore, the carbon catalyst was readily

Fig. 3. Preparation of the sulfonated carbon material [27]. (A) Pyrolysis; (B) carbonization; (C) Sulfonation.

separated from the saccharide solution after the reaction for reuse without a loss of activity.

This tactic for the design of a solid acid is widely used to find new efficient catalysts for cellulose conversion. Onda et al. [29] used a sulfonated activated carbon (AC) catalyst and obtained a 41% glucose yield with 95% selectivity after a 24 h reaction at 150 °C for the hydrolysis of cellulose. Using sulfonated silica-carbon nanocomposites Van de Vyver et al. [30] improved the glucose yield to 50% at 61% conversion of cellulose under similar reaction conditions. Furthermore, Pang et al. [31] reported a 75% glucose yield with 94% conversion of cellulose on sulfonated mesoporous carbon CMK-3.

Although many other solid acid catalysts such as layered niobium molybdate (HNbMoO_6) [32] and wormhole-type mesoporous $\text{Ta}_x\text{W}_{10-x}$ oxides [33] in addition to conventional solid acids like sulfonated zirconia, Amberlyst and Nafion were used for cellulose conversion, low catalytic activities have been obtained until now.

Recently, our group reported a carbon supported metal catalyst, Ru/CMK-3, for the hydrolysis of cellulose at 230 °C in a very short reaction time to prevent the deep degradation of the formed glucose [23]. Despite the moderate yield of glucose (ca. 30%), the turnover number (TON) of the catalyst was very high (145 based on bulk Ru) by comparison to those of the sulfonated carbon catalysts (1.6–5.1 based on sulfonated group). We observed a cooperative effect between CMK-3 and Ru, in which the main role of CMK-3 was to hydrolyze cellulose to oligosaccharides and Ru promoted the conversion of oligosaccharides to glucose. Our recent study confirmed that the Ru species was actually in an oxidized state, which acted as the real active site for the hydrolysis of oligosaccharides.

3 One-pot catalytic conversion of cellulose into valuable compounds

The catalytic conversion of cellulose using solid catalysts in a one-pot reaction system usually involves no less than three phases – cellulose, solid catalysts, a reaction medium like water or ionic liquids, and gases such as H_2 , O_2 , or air (some gases like CO , CO_2 , or light hydrocarbons can also be produced during this reaction). Clearly, since solid cellulose hardly gets involved in the catalytic cycles it needs to be dissolved in the liquid medium as an initial step for the formation of small molecules such as oligosaccharides and glucose, which can then contact the active species or sites on the catalyst surface where the catalytic reactions occur. Accordingly, we roughly divide the reaction process into two steps: the first is a catalytic or non-catalytic hydrolysis of cellulose into water-soluble saccharides including oligomers and glucose and the second consists of various

catalytic reactions such as hydrogenation, hydrogenolysis, and oxidation to produce sugar alcohols and organic acids. Based on this “two-step” viewpoint, the catalysts can be classified into two categories: (a) monofunctional catalysts for hydrogenation or hydrogenolysis and (b) a combination of acid catalysts with hydrogenation or hydrogenolysis catalysts.

3.1 Hydrogenation to hexitols

In 2006, our group discovered the conversion of microcrystalline cellulose to hexitols using supported noble metal catalysts [17]. Among the variety of metals examined, Pt and Ru proved to be the most effective for this process. For example, Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyzed the conversion of cellulose to yield 25% sorbitol and 6% mannitol (Fig. 4). Yan et al. [34] reported the conversion of cellobiose to hexitols in the presence of noble metal catalysts under pressurized H_2 . They found that Ru had the best hydrogenation ability for the production of sorbitol compared to the Pt, Pd, and Rh catalysts at pH = 2.

Since these milestone studies established a new field in the catalytic transformation of cellulose and related compounds, many researchers have contributed to the exploitation of more efficient catalysts or reaction systems for cellulose conversion. Luo et al. [21] used a carbon supported Ru catalyst and obtained a 30% yield of sorbitol and a 10% yield of mannitol at 245 °C at 6 MPa of H_2 pressure. They proposed that in situ-produced H^+ ions from HCW were responsible for the hydrolysis of cellulose into glucose, which underwent further hydrogenation to produce hexitols. Using carbon nanotubes as supports, Deng et al. [35] achieved a 69% yield of sorbitol using Ru catalysts.

Seeking effective base-metal catalysts is another strategy in the field of cellulose conversion. Ding et al. [36] reported

Fig. 4. Catalytic cellulose conversion into sorbitol and mannitol [17].

a 48% yield of sorbitol at 100% cellulose conversion at 225 °C and 6 MPa of H₂ pressure using a less expensive nickel phosphide catalyst, which unfortunately exhibited low stability during recycling because of the loss of active components. More interestingly, Van de Vyver et al. [22] designed a new Ni catalyst supported on carbon nanofibers (Ni/CNF), which entangled a cellulose matrix and facilitated the hydrogenation of released glucose on the Ni active phases that are attached to the top of the CNF. A sorbitol yield of 50% was obtained at 190 °C and 6 MPa of H₂ pressure, which was much higher than that using AC supported Ni catalysts.

Very recently, we reported on a specific hydrogenation system for cellulose transformation, i.e. transfer hydrogenation in which 2-propanol served as a hydrogen source to replace gaseous H₂ [37]. 2-Propanol was dehydrogenated to acetone and released as two active hydrogen species on the catalyst surface and the subsequent hydrogenation of glucose produced hexitols (Fig. 5). For instance, at 190 °C and after an 18 h reaction, a 43% yield of hexitols (34% sorbitol and 9% mannitol) was achieved on a Ru/AC (Norit) catalyst. Only a few fractions of the formed hydrogen species were used for the next hydrogenation and most of them were liberated to the gas phase in the form of H₂ with a partial pressure of 0.8 MPa over the initial 0.5 h period. Considering this phenomenon, we evaluated the hydrogenation of cellulose at a H₂ pressure as low as 0.8 MPa without 2-propanol on the same catalyst and gained good yields of sugar alcohols (sorbitol 30%, mannitol 8%). After characterization of the Ru/AC catalyst, it was interesting to find that tri- or tetra-valent Ru species were responsible for the high activity of the catalyst for the transfer hydrogenation whereas zero-valent Ru was inactive in this reaction.

3.2 Hydrogenolysis to ethylene glycol

Zhang and coworkers [38–42] reported the transformation of cellulose to ethylene glycol (EG) with high yields in the presence of a series of tungsten-based catalysts. They

Fig. 5. Transfer hydrogenation of cellulose to sugar alcohols [37].

developed carbon supported nickel-promoted tungsten carbide catalysts (Ni-W₂C/AC) to catalyze the reaction and produce EG in a 61% yield based on weight, and found that 2 wt% Ni played an important role in improving the activity and selectivity of the monometallic carbide. The following reasons were given for the catalytic enhancement: (1) modification of the bonding configuration of EG, thereby reducing the activity toward undesired decomposition; (2) a synergistic effect between Ni and W₂C. When combining group 8–10 transition metals and W as bimetallic catalysts the synergistic effect is still present for W and the other metal during the chain cracking of glucose and hydrogenation. A maximum yield of 75% EG was obtained over the Ni-W/SBA-15 catalyst. This study confirmed that W plays an important role in cracking the carbon chain into glucose. Even on tungsten phosphide a favorable EG yield was found for the cellulose conversion.

On the other hand, they observed a support effect for single tungsten carbides (WC_x), which gave an enhanced EG yield after dispersing on a new three-dimensional mesoporous carbon (MC), even comparable to that on 2 wt% Ni promoted WC_x, i.e. 73%, 48%, and 74% for WC_x/MC, WC_x/AC, and 2 wt% Ni-WC_x/MC, respectively [42]. The high catalytic performance was attributed to the unique and regular 3D structure of the interconnected mesopores of the carbon material and the resultant high dispersion of the tungsten carbide.

3.3 Combination of catalytic hydrolysis and hydrogenation

The strategy for most of the aforementioned studies is to develop various efficient catalysts for the hydrogenation or hydrogenolysis steps where water is responsible for hydrolyzing cellulose to soluble saccharides like glucose. Another strategy shown in some studies is to combine liquid/solid acid hydrolysis catalysts and metal catalysts for hydrogenation or hydrogenolysis.

Geboers et al. [43] integrated soluble heteropolyacids (H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀) and commercial Ru/C catalysts for the conversion of ball-milled cellulose and obtained 85% hexitol yields at 190 °C and 6 MPa of H₂ pressure within 1 h. Palkovits et al. [20] reported the conversion of α-cellulose at 160 °C over different mineral acids (H₂SO₄ and H₃PO₄) when combined with carbon-supported Pt, Pd, and Ru catalysts. They obtained a 60% yield for sugars and sugar alcohols with 84% selectivity at an α-cellulose conversion of 72%. Furthermore, the concept was successfully transferred to real feedstocks in the form of spruce reaching close to 60% conversion in 1 h.

However, the use of liquid acid in the above two cases is impractical even though good catalytic performance is ob-

tained. Joining a solid acid with an active metal catalyst is most promising.

3.4 Oxidation to gluconic acid

Gluconic acid is an important intermediate in the pharmaceutical and food industry, and can be produced by the catalytic oxidation of glucose with oxygen on supported Au [44,45], Pd-Bi/C catalysts [46], or Pt supported on sulfonated carbon [47].

Tan et al. [44] recently reported the selective oxidation of cellobiose into gluconic acid over CNT-supported gold nanoparticles. The catalytic process afforded a 68% yield of gluconic acid at an 81% cellobiose conversion. This aqueous phase oxidation of cellobiose was dependent on the presence of acidic functional groups on the nitric acid-pretreated surface of the CNT support.

Onda et al. [47] used a sulfonated carbon supported Pt catalyst (Pt/AC-SO₃H) for the oxidation of starch in air to realize a combination of solid acid for hydrolysis and metal catalysts for the oxidation step. A synergistic effect was observed between the acidic and metallic sites on the bi-functional catalysts.

Although the two examples provided herein refer only to the oxidation of cellobiose or starch, similar catalytic behavior would be conceivable starting from cellulose with reduced crystallinity or from soluble oligosaccharides that are released in hydrothermal or acidic treated cellulose [8].

4 Conclusions and prospects

Cellulose polymers are simply composed of repeat AGUs. The ubiquitous inter- and intra-molecular hydrogen bonds in the cellulose matrix do not only render the structure recalcitrant under ambient conditions but also lead to unfavorable product selectivity when the matrix is destroyed chemically to produce a pool of various compounds. The non-catalytic hydrolysis of cellulose by HCW is not product selective but it is a simple and convenient way to dissolve cellulose. One strategy to improve product selectivity is to design highly active and durable solid acids to dominate the hydrolysis process of cellulose. Another strategy is the combination of HCW (or a solid acid) with efficient solid metal catalysts where a two-step reaction system is established. The hydrolysis of cellulose by HCW (or a solid acid) provides intermediate saccharides including glucose units, which are promoted for further reactions such as hydrogenation, hydrogenolysis, or oxidation and this occurs on the efficient metal catalysts. The concerted effect between these two steps leads to a high selectivity for the target product. Based on this viewpoint, quite a few successful examples were reviewed. This work will help chemists ex-

ploit new efficient catalysts for various valuable products with high yields in the future.

References

- 1 Huber G W, Corma A. *Angew Chem, Int Ed*, 2007, **46**: 7184
- 2 Corma A, Iborra S, Velty A. *Chem Rev*, 2007, **107**: 2411
- 3 Dhepe P L, Fukuoka A. *Catal Surv Asia*, 2007, **11**: 186
- 4 Stöcker M. *Angew Chem, Int Ed*, 2008, **47**: 9200
- 5 Krässig H A. Cellulose: Structure, Accessibility, and Reactivity. Yverdon: Gordon and Breach Science Publishers, 1993. 26
- 6 Dhepe P L, Fukuoka A. *ChemSusChem*, 2008, **1**: 969
- 7 Rinaldi R, Schüth F. *ChemSusChem*, 2009, **2**: 1096
- 8 Van de Vyver S, Geboers J, Jacobs P A, Sels B F. *ChemCatChem*, 2011, **3**: 82
- 9 Swatloski R P, Spear S K, Holbrey J D, Rogers R D. *J Am Chem Soc*, 2002, **124**: 4974
- 10 Huber G W, Iborra S, Corma A. *Chem Rev*, 2006, **106**: 4044
- 11 Nisizawa K. *J Ferment Technol*, 1973, **51**: 267
- 12 Nishiyama Y, Sugiyama J, Chanzy H, Langan P. *J Am Chem Soc*, 2003, **125**: 14300
- 13 Yu Y, Wu H. *Ind Eng Chem Res*, 2010, **49**: 3902
- 14 Yu Y, Lou X, Wu H. *Energy Fuels*, 2008, **22**: 46
- 15 Akiya N, Savage P E. *Chem Rev*, 2002, **102**: 2725
- 16 Yu Y, Wu H. *Ind Eng Chem Res*, 2009, **48**: 10682
- 17 Fukuoka A, Dhepe P L. *Angew Chem, Int Ed*, 2006, **45**: 5161
- 18 Jollet V, Chambon F, Rataboul F, Cabiacc A, Pinel C, Guillon E, Essayem N. *Green Chem*, 2009, **11**: 2052
- 19 Jollet V, Chambon F, Rataboul F, Cabiacc A, Pinel C, Guillon E, Essayem N. *Top Catal*, 2010, **53**: 1254
- 20 Palkovits R, Tajvidi K, Procelewska J, Rinaldi R, Rupper A. *Green Chem*, 2010, **12**: 972
- 21 Luo C, Wang S A, Liu H C. *Angew Chem, Int Ed*, 2007, **46**: 7636
- 22 Van de Vyver S, Geboers J, Dusselier M, Schepers H, Vosch T, Zhang L, Van Tendeloo G, Jacobs P A, Sels B F. *ChemSusChem*, 2010, **3**: 698
- 23 Kobayashi H, Komanoya T, Hara K, Fukuoka A. *ChemSusChem*, 2010, **3**: 440
- 24 Kobayashi H, Ito Y, Komanoya T, Hosaka Y, Dhepe P L, Kasai K, Hara K, Fukuoka A. *Green Chem*, 2011, **13**: 326
- 25 Toda M, Takagaki A, Okamura M, Kondo J N, Hayashi S, Domen K, Hara M. *Nature*, 2005, **438**: 178
- 26 Suganuma S, Nakajima K, Kitano M, Yamaguchi D, Kato H, Hayashi S, Hara M. *J Am Chem Soc*, 2008, **130**: 12787
- 27 Okamura M, Takagaki A, Toda M, Kondo J N, Domen K, Tatsumi T, Hara M, Hayashi S. *Chem Mater*, 2006, **18**: 3039
- 28 Yamaguchi D, Kitano M, Suganuma S, Nakajima K, Kato H, Hara M. *J Phys Chem C*, 2009, **113**: 3181
- 29 Onda A, Ochi T, Yanagisawa K. *Green Chem*, 2008, **10**: 1033
- 30 Van de Vyver S, Peng L, Geboers J, Schepers H, De Clippel F, Gommers C J, Goderis B, Jacobs P A, Sels B F. *Green Chem*, 2010, **12**: 1560
- 31 Pang J, Wang A, Zheng M, Zhang T. *Chem Commun*, 2010, **46**: 6935

- 32 Takagaki A, Tagusagawa C, Domen K. *Chem Commun*, 2008: 5363
- 33 Tagusagawa C, Takagaki A, Iguchi A, Takanabe K, Kondo J N, Ebitani K, Tatsumi T, Domen K. *Chem Mater*, 2010, **22**: 3072
- 34 Yan N, Zhao C, Luo C, Dyson P J, Liu H, Kou Y. *J Am Chem Soc*, 2006, **128**: 8714
- 35 Deng W P, Tan X S, Fang W H, Zhang Q H, Wang Y. *Catal Lett*, 2009, **133**: 167
- 36 Ding L, Wang A, Zheng M, Zhang T. *ChemSusChem*, 2010, **3**: 818
- 37 Kobayashi H, Matsushashi H, Komanoya T, Hara K, Fukuoka A. *Chem Commun*, 2011, **47**: 2366
- 38 Ji N, Zhang T, Zheng M, Wang A, Wang H, Wang X, Chen J G. *Angew Chem, Int Ed*, 2008, **47**: 8510
- 39 Ji N, Zhang T, Zheng M, Wang A, Wang H, Wang X, Shu Y, Stottemyer A L, Chen J G. *Catal Today*, 2009, **147**: 77
- 40 Zheng M, Wang A, Ji N, Pang J, Wang X, Zhang T. *ChemSusChem*, 2010, **3**: 63
- 41 Zhao G, Zheng M, Wang A, Zhang T. *Chin J Catal*, 2010, **31**: 928
- 42 Zhang Y, Wang A, Zhang T. *Chem Commun*, 2010, **46**: 862
- 43 Geboers J, Van de Vyver S, Carpentier K, De Blochouse K, Jacobs P, Sels B. *Chem Commun*, 2010, **46**: 3577
- 44 Tan X, Deng W, Liu M, Zhang Q, Wang Y. *Chem Commun*, 2009: 7179
- 45 Ishida T, Kinoshita N, Okatsu H, Akita T, Takei T, Haruta M. *Angew Chem, Int Ed*, 2008, **47**: 9265
- 46 Biella S, Prati L, Rossi M. *J Catal*, 2002, **206**: 242
- 47 Onda A, Ochi T, Yanagisawa K. *Catal Commun*, 2011, **12**: 421