



Efficient valorization of biomass to biofuels with bifunctional solid catalytic materials

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ARTICLE INFO

Article history:

Received 29 July 2015

Accepted 20 April 2016

Available online 17 May 2016

Keywords:

Lignocellulose

Catalyst design

Catalysis

One-pot reaction

Platform chemicals

Nanotechnology

ABSTRACT

Mono-functional catalytic materials are used for many types of chemical transformations, but are tedious for delivering products from multiple-step reactions required for the valorization of biomass. An emerging trend is to integrate catalytic transformations, reaction engineering and product separation into a single operation, wherein catalyst design is considered as the key approach to develop efficient, low energy and environmentally-friendly reaction systems. Bifunctional solid catalysts open a door for carrying out domino/cascade- and tandem/sequential-type reactions in a single pot, for which the number of isolation or purification steps can be lessened or eliminated so that removal of unwanted by-products becomes unnecessary. This review introduces bifunctional materials used in one-pot multiple transformations of biomass into biofuels and related chemicals. Emphasis is placed on the assessment of the bifunctionality of catalytic materials, including Bronsted–Lewis acid, acid–base, and metal particles–acid or base bifunctional catalysts with some discussion being on combined catalytic systems with electrochemical, chemo-enzymatic and photochemical methods. Plausible reaction mechanisms for key pathways are shown. Relevant auxiliaries to boost catalytic activity and product selectivity, such as reaction media, heating modes and morphological properties of the catalytic materials are analyzed. Use of appropriate bifunctional catalytic materials provides many opportunities for design of highly efficient reaction systems and simplified processing for producing biofuels and chemicals from lignocellulosic biomass.

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Abbreviations: AC, activated carbon; AgSTA, silver exchanged silicotungstic acid; APPO, aqueous phase partial oxidation; ATP, attapulgitic; 1,4-BDO, 1,4-butanediol; BG, 1,4-butylene glycol; BHMF, 2,5-bis(hydroxymethyl)furan; BHMTF, 2,5-bis(hydroxymethyl)tetrahydrofuran; BMF, 5-bromomethylfurfural; [BMIM]Cl, 1-butyl-3-methylimidazolium chloride; BS, benzene sulfonate; BV, Baeyer–Villiger; CFP, catalytic fast pyrolysis; CMF, 5-chloromethylfurfural; CNFs, carbon nanofibers; CNT, carbon nanotube; Coni, α -conidendrin; ConiA, α -conidendric acid; CP, chloromethyl polystyrene; Cu-BTC, copper benzene-1,3,5-tricarboxylate; CVD, catalytic vapor deposition; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DFF, 2,5-diformylfuran; DFT, density functional theory; DHA, dihydroxyacetone; DHH, 2,5-dihydroxyhexane; DMA, N,N-dimethylacetamide; DMF, 2,5-dimethylfuran; DMSO, dimethylsulfoxide; DMTHF, 2,5-dimethyltetrahydrofuran; DS, dodecyl sulfate; DVB, divinylbenzene; EDX, energy-dispersive X-ray spectroscopy; EG, ethylene glycol; EL, ethyl levulinate; EMF, 5-ethoxymethylfurfural; [EMIM]Cl, 1-ethyl-3-methylimidazolium chloride; F₂C, 1,4-pentandien-3-on-1,5-di-2-furanyl; FAc, 4-(2-furyl)-3-buten-2-on; FAMES, fatty acid methyl esters; FDCA, 2,5-furandicarboxylic acid; FDMC, 2,5-dimethylfuroate; Fe³⁺-POP-1, Fe³⁺-porous organic polymer; Fe-BTC, iron benzene-1,3,5-tricarboxylate; FfA, furfuryl alcohol; FFAs, free fatty acids; FFCA, 5-formyl-2-furancarboxylic acid; FT-IR, Fourier transform infrared spectroscopy; GC-MS, gas chromatography–mass spectrometry; GLY, glyceraldehyde; GO, graphene oxide; GVL, γ -valerolactone; HAA, hydroalkylation/alkylation; HAP, hydroxylapatite; HDO, hydrodeoxygenation; HHD, 5-hydroxy-2,5-hexanedione; HMF, 5-hydroxymethylfurfural; HMFC, 5-hydroxymethyl-2-furancarboxylic acid; HMMF, 5-hydroxymethyl methylfuroate; HMR, hydroxymatairesinol; HNTs, halloysite nanotubes; HOAc, acetic acid; HPAs, heteropoly acids; HPLC, high-performance liquid chromatography; HT, hydrotalcite; HTFA, trifluoroacetic acid; ICP-AES, inductively coupled plasma-atomic emission spectroscopy; ILs, ionic liquids; LA, levulinic acid; LAS-OH, Lewis acid site-OH; MA, maleic anhydride; MC, mesoporous carbon; MF, 2-methylfuran; MFA, methyl furoate; MFFA, 5-methylfurfuryl alcohol; MFF, methyl 5-formyl-2-furoate; MFF, 5-methylfurfural; MIBK, methyl isobutyl ketone; [MIMPS]₃PW₁₂O₄₀, 1-(3-sulfonic acid)propyl-3-methyl imidazolium phosphotungstate; ML, methyl levulinate; MOF, metal organic framework; MSNs, mesoporous silica nanoparticles; MTHF, 2-methyltetrahydrofuran; NA-p, niobium hydroxide treated with 1 M phosphoric acid; NHC, N-heterocyclic carbene; oxoMAT, oxomatairesinol; P[BVIM]Cl, poly(3-butyl-1-vinylimidazolium chloride); PAL, pyruvic aldehyde; PBF, poly(butylene 2,5-furandicarboxylate); PMIM, propyl-3-methylimidazolium; POM, polyoxometalate; PON1, paraoxonase I; PVP, polyvinyl pyrrolidone; ROP, ring opening products; SA, succinic acid; SAPO, silicoaluminophosphate; SC, supercritical; SZ, sulfated zirconia; TA-p, tantalum hydroxide treated with 1 M phosphoric acid; TBAC, tetrabutylammonium chloride; TEAB, tetraethylammonium bromide; TEMPO, 2,2,6,6-tetramethyl-piperidin-1-oxyl; TEOS, tetraethoxysilane; TGA, thermogravimetric; THF, tetrahydrofuran; THFA, tetrahydrofurfuryl alcohol; TiZ, titania zirconia; TRS, total reducing sugar; TS, TiO₂–SiO₂; VPO, vanadium phosphate; WC_x, tungsten carbide; WP, tungsten phosphide; WZ, tungstated zirconia; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; ZrC, zirconium carbonate.

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<http://dx.doi.org/10.1016/j.pecs.2016.04.004>

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1. Introduction

Lignocelluloses composed of chitosan, lipids, microalgae, macroalgae, polyols or polysaccharide and lignin units are the dominant biomass resources in the environment [1]. Microbial, thermochemical, and chemical/catalytic processes are three main approaches of converting biomass into energy, biofuels or chemicals [2]. Enzyme-mediated catalytic processes are the most common way to produce bioethanol, butanol and biodiesel, in which pretreatment and post-treatment steps are used to remove compounds toxic to the microorganisms. Thermal processing of biomass gives syngas via steam gasification by partial oxidation at temperatures from ~800 to 1000 °C [3] or bio-oil via fast pyrolysis with or without catalyst at temperatures of ~500 °C [4,5]. Efficient processes for the

catalytic upgrading of both syngas and bio-oil to transportation fuels are in high demand [6,7]. At lower reaction temperatures (ca. 300 °C), thermal processing of biomass with catalytic methods offers the possibility of selectively yielding a narrow range of products and to reduce the energy requirements of the transformations [8–10]. Traditional catalytic strategies have relied mainly on mono-functional materials for chemical transformations and while they are able to deliver the desired products for a wide range of substrates, they lack efficiency when dealing with complex molecules [11–13]. Bifunctional solid catalysts provide a method for efficiently transforming complex substrates into products since they integrate sequential catalytic steps and avoid by-product formation and separation [14–16].

In organic synthesis, bifunctional catalysis denotes simultaneous activation of both partners of a bimolecular reaction [17].

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