Review

Hydrodeoxygenation processes: Advances on catalytic transformations of biomass-derived platform chemicals into hydrocarbon fuels

Sudipta De [a,*], Basudeb Saha [a,b], Rafael Luque [c]

[a] Laboratory of Catalysis, Department of Chemistry, University of Delhi, North Campus, Delhi 110007, India
[b] Department of Chemistry and the Center for Direct Catalytic Conversion of Biomass to Bioenergy (C3Bio), Purdue University, West Lafayette, IN 47906, USA
[c] Departamento de Quimica Organica, Universidad de Cordoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV-A, Km 396, 14014 Cordoba, Spain

HIGHLIGHTS

- Strategies for the catalytic conversion of platform molecules.
- Thermo-chemical processes aimed to fuels production.
- Catalysts development and design.
- Technologies for fuels conversion from biomass.

ARTICLE INFO

ABSTRACT

Lignocellulosic biomass provides an attractive source of renewable carbon that can be sustainably converted into chemicals and fuels. Hydrodeoxygenation (HDO) processes have recently received considerable attention to upgrade biomass-derived feedstocks into liquid transportation fuels. The selection and design of HDO catalysts plays an important role to determine the success of the process. This review has been aimed to emphasize recent developments on HDO catalysts in effective transformations of biomass-derived platform molecules into hydrocarbon fuels with reduced oxygen content and improved H/C ratios. Liquid hydrocarbon fuels can be obtained by combining oxygen removal processes (e.g. dehydration, hydrogenation, hydrogenolysis, decarbonylation etc.) as well as by increasing the molecular weight via C–C coupling reactions (e.g. aldol condensation, ketonization, oligomerization, hydroxyalkylation etc.). Fundamentals and mechanistic aspects of the use of HDO catalysts in deoxygenation reactions will also be discussed.

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1. Introduction

Declining fossil fuel resources, along with the increased petroleum demand by emerging economies, drives our society to search for new sources of liquid fuels. With decreasing crude-oil reserves, increased political and environmental concerns about the use of fossil-based energy carriers, the focus has recently turned towards an improved utilization of renewable energy resources. Biomass is a highly abundant and carbon–neutral renewable energy resource, being an ideal alternative option for the production of biofuels using different catalytic technologies from conventional petroleum refinery processing. During the last decade, innovative protocols have been developed for the production of biofuels from sustainable resources. Several fuel components have been identified and tested by means of biomass valorization. The results have been already summarized in recent overviews in past years (Huber and Corma, 2007; Alonso et al., 2010; Climent et al., 2014). Based on the aforementioned premises, the proposed contribution has been aimed to emphasize the critical and fundamental role of innovative and newly reported catalytic systems in the HDO process. The role of active catalyst functions has been discussed with their interconnected mechanistic insights.

Lignocellulose is the major non-food component of biomass comprising three main fractions, namely cellulose (40–50%), hemicellulose (25–35%) and lignin (15–20%). Cellulose is a polymer of glucose units linked by β-glycosidic bonds which can lead to important building blocks (e.g. levuninic acid, 5-hydroxymethylfurfural) upon pretreatment via hydrolysis followed by dehydration. Hemicellulose is comparably composed of C_5 and C_6 sugar

* Corresponding author at: Laboratory of Catalysis, Department of Chemistry, University of Delhi, North Campus, Delhi 110007, India.
E-mail addresses: sudiptade22@gmail.com (S. De), q62alsor@uco.es (R. Luque).

monomers including D-xylose, D-galactose, D-arabinose, D-glucose and D-manose as major compounds. Lignin is the most complex and recalcitrant fraction, having a three-dimensional randomised aromatic structure responsible for the structural rigidity of plants.

Three main existing routes for lignocellulosic processing into fuels and chemicals include gasification, pyrolysis and pretreatment/hydrolysis. Gasification and pyrolysis are pure thermal routes aimed to convert lignocellulose into syngas and liquid fractions (bio-oils) which are valuable intermediates for the production of fuels and chemicals. However, the harsh temperature conditions employed in these routes difficult a proper control of reaction chemistries producing intermediate fractions with high degrees of impurities that require deep cleaning and/or conditioning prior to upgrading to valuable products.

Pretreatment/hydrolysis routes allow separation/fractionation of lignin and carbohydrate fractions of lignocellulose. The sugar fraction can be subsequently processed to fuels and chemicals using (bio)chemical and biological routes whereas lignin is typically burnt to provide heat and electricity for various processes. Separate catalytic treatments of the different fractions (namely hemicellulose and cellulose) can provide access to different platform chemicals. Following the production of platform chemicals, various catalytic strategies have been developed for their upgrading into fuels.

Biomass-derived platform molecules are generally highly oxygenated compounds and their conversion into liquid hydrocarbon fuels needs oxygen removal reactions. New catalytic routes and mechanistic insights are required to develop advanced methods for a chemically controllable disassembly of biopolymers as well as subsequent selective deoxygenation of resulting feedstocks (Rinaldi and Schuth, 2009; Huber et al., 2006). Different methods including dehydration, hydrogenolysis, hydrogenation, decarbonylation, decarboxylation have been reported to remove oxygen functionalities. Diesel range hydrocarbons can also be obtained by increasing the carbon number via C–C coupling reactions through different chemistries including aldol-condensation, ketonization, oligomerization and hydroxyalkylation. A major challenge in converting biomass into hydrocarbon fuels relates to an efficient cleavage of ubiquitous ether and alcoholic C–O linkages within the feedstock molecules to reduce both the oxygen content and degree of polymerization.

Hydrodeoxygenation (HDO) can be currently considered as most effective method for bio-oil upgrading which improves the effective H/C ratio, eventually leading to hydrocarbons. The key challenge of HDO processes is to achieve a high degree of oxygen removal with minimum hydrogen consumption, for which catalysts need appropriate and careful designed. Up to now, several classes of catalysts have been reported for HDO, with various advantages and disadvantages (He and Wang, 2012). Precious metal catalysts (e.g., Pd, Pt, Re, Rh, and Ru) and non-precious metal catalysts (e.g., Fe, Ni and Cu) have exhibited good activities in hydrogenation/hydrogenolysis reactions. However, the proposed systems require high hydrogen pressures that result in excessive hydrogen consumption, leading to complete hydrogenation of double bonds in some systems (Bykova et al., 2012).

Industrial catalysts based on Co–Mo–Ni formulations can provide a comparatively superior HDO performance but these undergo rapid deactivation due to coke formation and water poisoning (Badawi et al., 2011). Since HDO reactions generally require high pressures of hydrogen, a selective HDO catalyst is highly desirable in order to prevent complete hydrogenation of unsaturated compounds as well as to prevent over-utilization of expensive hydrogen. In the light of these premises, cost effective and simple catalytic routes combined with advanced highly active and stable (nano) catalytic systems are required for a large scale commercial development of lignocellulosic biofuels.

This contribution summarizes recent advances in HDO processes for the transformation of biomass-derived feedstocks into liquid transportation fuels (Scheme S1).

2. HMF platform for hydrocarbon fuels

5-Hydroxymethylfurfural (HMF) is a highly reactive biomass-derived compound with a challenging hydrogenation/hydrogenolysis profile due to the presence of several functionalities in its structure including double bonds, hydroxyl and carbonyl groups (Nakagawa et al., 2013). HMF reductive chemistries include C=O bond reduction, hydrogenation of the furan ring as well as C–O hydrogenolysis. In this section, we will mainly discuss a number of key proposed catalytic technologies for hydrogenation and C–C coupling reactions followed by HDO to upgrade HMF into higher energy hydrocarbons.

2.1. Hydrogenation of HMF

2,5-Dimethylfuran (DMF) has received increasing attention in recent years as promising liquid transportation biofuel. DMF can be obtained via selective hydrogenation of biomass-derived HMF. Compared to current market-leading bioethanol, DMF possesses a higher energy density, higher boiling point and a higher octane number, being also immiscible with water. Studies on selective hydrogenation of HMF into DMF are becoming highly relevant in the field of bioenergy. Production strategies of DMF from HMF have been recently reviewed by Hu et al. (2014).

The Dumesic group studied and evaluated the different possible strategies to upgrade HMF into liquid fuels (Alonso et al., 2010). The breakthrough of deriving DMF from biomass-derived fructose was firstly reported in a two-step process (Roman-Leshkov et al., 2007). The first step involved an acid-catalyzed dehydration of fructose (30 wt%) in a biphasic reactor to produce HMF, followed by subsequent hydrogenation over a supported bimetallic Cu–Ru/C catalyst using molecular hydrogen (H_2) in 1-butanol. The initial hydrogenation reactions were carried out in the presence of copper chromite ($CuCrO_4$) catalysts. This catalyst was however shown to be easily deactivated by chloride ions even at ppm level. The low melting point and high surface mobility of Cu(I) chloride species were observed to accelerate Cu catalysts sintering. To overcome this problem, a chloride-resistant carbon-supported copper–ruthenium (Cu–Ru/C) catalyst was developed. Based on literature reports, copper has a comparably lower surface energy to that of ruthenium and their combination generates a two-phase system in which the copper phase coats the ruthenium surface as confirmed by electron spectroscopy. The designed Carbon-supported Ru catalyst is resistant to deactivation by chloride ions, while Cu shows the predominant role in hydrogenolysis over Ru. Cu–Ru/C catalyst consequently exhibits copper-like hydrogenolysis behavior combined with ruthenium-like chlorine resistance. The liquid-phase hydrogenation of HMF using Cu–Ru/C catalyst provided quantitative conversion of HMF with a maximum 71% DMF selectivity under 6.8 bar H_2 in 1-butanol (Table 1). The authors demonstrated no deactivating effect of chloride ions when the reaction was repeated in the presence of 1.6 mmol/L chloride ions. After this pioneering work, many groups have attempted DMF synthesis using different approaches.

The same catalytic system (Cu–Ru/C, hydrogen and 1-butanol) was also explored for the selective hydrogenation of crude biomass-derived HMF from corn stover (Binder and Raines, 2009). A 49% DMF yield from HMF was achieved at 220 °C after 10 h, which further proved a wide applicability of Cu–Ru/C in the selective hydrogenation of HMF to DMF, although the activity of the