Angewandte Chemie International Edition

Zeolites in Biorefineries

DOI: 10.1002/anie.201400922

Will Zeolite-Based Catalysis be as Relevant in Future Biorefineries as in Crude Oil Refineries?

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Dedicated to the MPI für Kohlenforschung on the occasion of its centenary

biomass conversion · biorefinery · heterogeneous catalysis · zeolites

Catalytic Functionalization of Petroleum Fractions with Zeolite Catalysts in Fossil Oil Refineries

Since half a century, synthetic zeolites became technological and scientific successful in the catalytic treatment of crude oil fractions, their role being connected to the particularly high Brønsted acidity in a crystalline matrix with porosity of molecular dimensions.[1] Although over 200 zeolite frameworks are available,[2] zeolite-catalyzed processes[3] use only about 10 different framework types.[1a]

In fossil oil refineries, acid zeolite catalysis aims at affecting the skeleton and functionality of hydrocarbon fractions through acid (monofunctional) cracking. Loaded with noble metals and in presence of hydrogen, the (bifunctional) catalysts perform hydrocracking. With metal sulfide-loaded bifunctional catalysts (hydrotreating), hydrocarbon defunctionalization occurs simultaneously (Figure 1). Reactions occur mostly in vapor phase, requiring thermostability of the zeolite catalyst during reaction, and high hydrothermal stability during regeneration or coke removal.[1,4]

Steam-stable or ultrastable Y zeolites (H-USY)[5] form the basis of innovative technology practicing fluid catalytic cracking of naphtha fractions.[6] The main catalytic actions of H-USY consist of hydrocarbon chain rearrangements and functional changes resulting from bimolecular hydrogen transfer reactions, yielding high gasoline yields rich in aromatics and with octane boosting properties. In the smaller pores of H-ZSM-5 cracking catalysts, only monomolecular cracking reactions are possible, reducing average size of, and functional changes in products.[7] The interaction between the pore surface of H-ZSM-5 and reactants is enhanced, resulting from a tighter fit between reaction transition state and zeolite voids by confinement and solvation effects.[8]

Hydroisomerization/hydrocracking of naphtha fractions is a flexible process in which reactor temperature changes of a few degrees produce a slate of products varying from gasoline and diesel, to jet and domestic fuels.[9] Pt on H-USY and H-Beta are bifunctional, assuring deprotonation and fast hydrogenation of formed intra-framework carbocations, rather than hydrogen transfer by bimolecular reactions. Conversion of alkanes shows ideal bifunctional catalysis[9,10] involving central chain branching of key importance in catalytic dewaxing processes. Central hydrocracking by single C−C bond scission reduces hydrocarbon chain lengths, important for reduction of the pour point temperature of waxy hydrocarbon fractions.

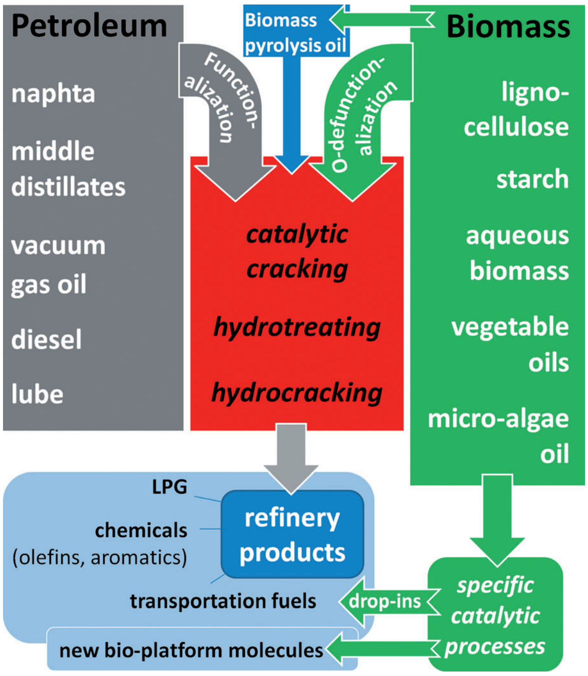

Figure 1. Overview of substitution of biomass (components) for petroleum fractions in important catalytic processes of crude oil refineries and specific processing to drop-ins or platforms.

Major Biomass Compounds and Properties

Major compound classes (Table 1) in woody biomass consist of cellulose, hemi-cellulose and lignin.[11] Non-fossil carbon is also contained in the triglyceride molecules of non-edible vegetable and microalgae oil.[12] Occasionally, starch is available from residues and wastes of certain food crops.[13] Chemical composition and physical appearance of biomass classes evidently will determine ultimate (catalytic) transformation routes.[14]

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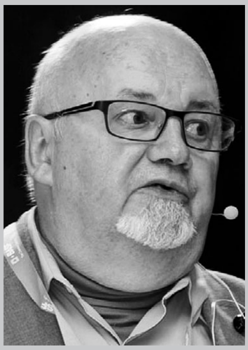
Table 1: Major biomass sources and elementary compound properties.

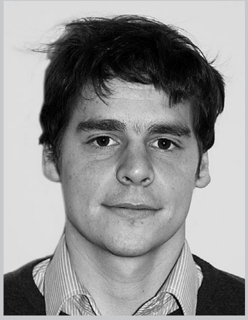
Biomass source	Compound class	Chemical structure	Typical properties
woody materials *straw, saw dust, bagasse, cornstover*	cellulose	linear glucose biopolymer with multiple inter-/intra-chain H-bonds	crystalline, recalcitrant towards catalytic hydrolysis
	hemicellulose	branched biopolymer of pentoses and hexoses	complex nature, amorphous
	lignin	branched biopolymer of phenolic allylic alcohols	amorphous, resistant towards catalytic/enzymatic hydrolysis
non-edible vegetable oils	triglycerides	triester of glycerol and fatty acids	1st generation biodiesel
microalgae oil	triglycerides	triester of glycerol and fatty acids	2nd generation biodiesel
sugar crop waste	starch, sugars	glucose polymer, mono-disaccharides	amorphous

Biomass in Petroleum Refineries

Figure 1 also shows an overview of conversion strategies for several biomass compound classes fed to three major catalytic refinery processes. Oxygen defunctionalization of sugars, triglycerides and alkylphenolics by hydrocracking/hydrotreating will dominate. Specific design of hydrotreating catalysts for trace removal of S and N, and for hydrogenation of (poly)aromatics with biomass compound feedstock becomes obsolete. This may require different catalyst properties and balance of acidity and metal functions. Obviously, possible absence of metal pre-sulfidation may allow implementation of Pt-Pd/H-zeolites. The scheme also suggests that a traditional petroleum-refinery can accept mixtures of crude oil and biomass, allowing the 20% substitution of fossil with renewable energy, as required by an EU directive.[15]



Pierre A. Jacobs is since 2008 professor emeritus with special mandate at KU Leuven. During his active career, he has been professor of Physical-Chemistry and Catalysis at KU Leuven and authored over 650 reviewed papers. The industrial impact of his research is visible in numerous patents and culminated in the nomination for the 2013 Alwin Mittasch special prize marking the centennial commissioning of the first ammonia plant. Among the awards received are the Paul Emmett Award, the Donald Breck Award, the Synetix Award, and the Kreitman Award.



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Bert F. Sels obtained his Ph.D. in 2000 at KU Leuven in the field of oxidation chemistry with heterogeneous catalysis. He was awarded the DSM Chemistry Award in 2000, and in 2005 the Incentive Award by the Societé Chimique Belge for his research achievements. In 2005 he was appointed assistant professor at KU Leuven, and full professor in 2008. His current research focuses on the synthesis, characterization and use of heterogeneous catalysis, mainly in transformation of renewable resources to chemicals.

The debate already started on the substitution of fossil hydrocarbons in oil refineries.[16] An indirect entrance of different biomass types into a classical refinery is possible by using catalytic fast pyrolysis (CFP), yielding bio-oils with comparable properties, irrespective of the type of H-ZSM-5 catalyst used.[17] Enhanced fuel properties are obtained with Ga/H-ZSM-5 bifunctional zeolites, in which Ga sites are responsible for decarbonylation and aromatization, whereas acid sites catalyze oligomerization.[18]

Other specific catalytic processes are available for the transformation of biomass compounds in a refinery environment, yielding fuel drop-ins and new bio-platform molecules (Figure 1).[19] Selecting the right platform molecule is challenging, as its synthesis should be straightforward and allow for feedstock flexibility while in itself, it should be a precursor of a wide range of products. Whereas glucose is a major bio-platform,[20] other notorious examples include 5-(hydroxymethyl)furfural (HMF), levulinic acid, lactic acid and glycerol.[21] Tools for their selection have recently been proposed.[22] The use of zeolites in the synthesis and upgrading of these molecules is an actively expanding field, using Lewis acidic[23] or bifunctional zeolite catalysts.[24] Although reviews partially cover this field,[14,25] an insightful comparison between zeolite-based petrochemical and bio-platform chemical upgrading with details on how the key zeolite concepts (e.g. shape selectivity) are transferred, is lacking today.

Biomass Defunctionalization in Integrated Biorefineries

Biomass conversion in integrated biorefineries containing pyrolysis-based, hydrothermal process-based, and fermentation-based technology, will yield biofuels, bio-oils, biogas, and

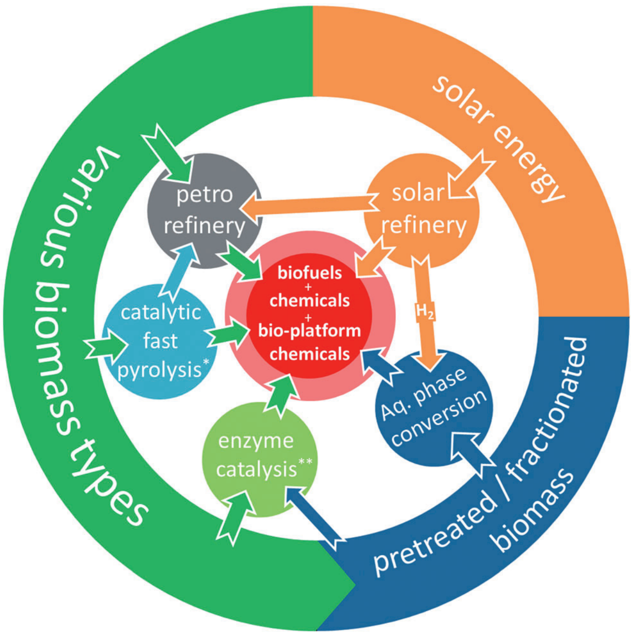

Figure 2. Concept of an integrated biorefinery. * Non-catalytic pyrolysis/gasification could be included. ** Zeolite-supported enzymes could be envisioned.

also bio-chemicals.[26] Research is currently intense on the utilization and the integrated processing of biomass feedstocks (Figure 2),[27] and the role of (zeolite)catalyzed chemical processes is prominent therein.[28]

New in a biorefinery environment is the direct formation of high yields of platform molecules from biomass components. Their oxygen content gives them low volatility, high solubility in water, high reactivity and low thermal stability, properties favoring catalytic processing by catalytic aqueous-phase technologies at moderate temperatures.[29]

In the present context, the shale gas and tight oil "revolution", although referring to fossil carbon and a not very sustainable technology at this moment, should be mentioned as it may become a game changer in the refinery (and chemical industry).[30] Unlike most crude oils, shale oils have high paraffin content[31] with hydrocarbon chains well over 50 C carbons. It will require specific refinery processing, analogous to that of Fischer–Tropsch liquids (waxes), catalytically upgradable by hydrocracking and hydroisomerization with Pt on H-zeolites.[32] It has been argued that shale gas may provide opportunities for production of bio-fuels (and bio-based chemicals) and may be at the basis of the availability of large quantities of hydrogen.[30] Ultimately, sustainable technologies for hydrogen production should take over, powered by energy from "solar refineries" (Figure 2).[33] In the search for hydrogen, the potential of zeolites is being investigated.[34] Catalytic steam reforming of bio-ethanol with Ni/Cs-Y, and photocatalytic water splitting with zeolite-supported TiO_2 and CdS, seem promising. Worth mentioning is aqueous reforming with Pt/alumina catalysts, forming increasing amounts of sustainable hydrogen along the following sequence of new bio-based platform molecules: glucose < sorbitol < glycerol < ethylene glycol (< methanol).[35] Aqueous reforming with Pt on H-zeolites has been overlooked.[24] Given their well-known, and compared to Pt on alumina, superior performance in hydrocarbon conversion, research on the design of zeolite-based (bifunctional) reforming catalysts looks timely.

Direct synthesis of bio-platform molecules from woody biomass, can occur by aqueous-phase catalytic conversion. The feasibility of conversion of concentrated aqueous starch solutions with bifunctional zeolites was already established in 1989,[36] and realized for concentrated cellulose gels two decades later.[37] The starch chain undergoes hydrolysis in aqueous solution with acid protons at the external zeolite crystal surface, the formed glucose being hydrogenated to high yields of sorbitol by intrazeolitic Ru clusters. As at the reaction temperature caramel formation from glucose is possible, relatively rapid hydrogenation with reference to hydrolysis should be realized by a proper balance of the acid and metal functions of the catalyst. Cellulose chains can also be hydrolyzed into glucose oligomers, after addition of the right trace amounts of mineral acid. Added Ru/H-USY generates a catalytic system, which after balancing of the two catalytic functions, yields high amounts of hexitols (Figure 3).

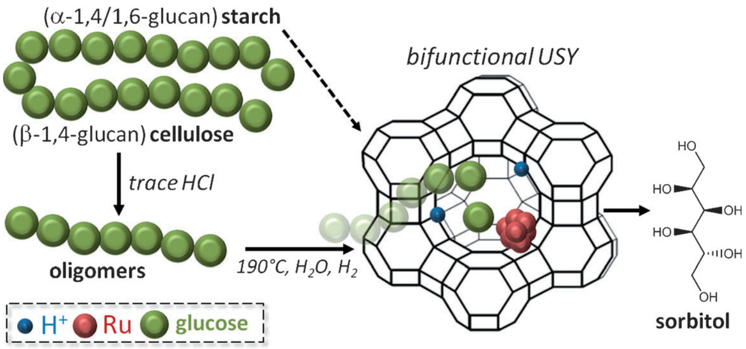

Figure 3. Bifunctional conversion of concentrated aqueous starch[36] and cellulose[37] at 190 °C with Ru on steamed NH_4Y zeolites.

In presence of H-zeolites, cellulose as such is partially susceptible to liquid-phase hydrolysis into glucose and HMF, the restricted pore size of H-MOR and H-Beta zeolites limiting glucose polymerization into humic acid species.[38]

Lignin reduction with classical hydrodesulfurization or specifically designed hydrodeoxygenation (HDO) catalysts, i.e. Ni/Mo on alumina, yields bio-oils rich in (alkyl)phenolics and aromatics.[39] In particular H-ZSM-5 is suited for cracking of lignin or ligno-cellulosic biomass, targeting biofuels (and bio-chemicals).[40] HDO studies with lignin model compounds show the potential of Pd/H-Beta zeolites.[41]

Of three main transformation approaches to microalgae oil catalytic refining,[42] bifunctional catalytic HDO with metals on H-zeolites, such as Ni or Pt-Re particles on H-ZSM-5 or Ni nanoparticles on H-Beta,[12] directly yields diesel-range alkanes. Otherwise, H-zeolites show high potential in selective ketonization of biomass carboxylic acids, as they seem to promote surface acyl rather than carboxylate species.[43]

The Role of Dealumination versus Desilication of H-Zeolites for Biomass Conversion

In a petro-refinery, thermally and hydrothermally stable zeolites are needed, while in integrated biorefineries several of the catalytic biomass transformation steps such as hydrolysis require catalyst stability in hot liquid water. Occasionally, stability should be retained after addition of small quantities of mineral acid.[37]

Hydrothermal calcination (or steaming) of H- or NH_4^+-zeolites, or strong acid treatment of H- and cation-exchanged zeolites, will cause lattice dealumination, yielding steam-stable materials. Depending on treatment severity, formed lattice defects and terminal silanol nests will be healed to different extent by silica migration, yielding extra-framework Al_xO_y species and a secondary mesopore system (25–30 nm).[44] Visualization of the interior of USY zeolites[45] shows that mesopores are fragmenting the zeolite crystal into microporous domains. Whereas part of the mesopores is linking micropore domains with the extragranular space, others show restricted orifices or are even blocked. The ultimate acidity for mono- and bifunctional catalysis would require a treatment that yields maximal dispersion of zeolitic domains into a regular network of open mesopores. Although less effort has been devoted to the steam-stability study of more dense zeolites, a similar picture is emerging for steamed H-ZSM-5,[46] and H-Mordenite.[47]

Treatment of H-USY zeolites with base,[48] catalyzes siloxane bridge hydrolysis, resulting in formation of 3 nm mesopores.[49] The final zeolite porosity is trimodal, containing micropores from synthesis, large mesoporous from steaming and/or acid leaching, and smaller "sponge-like" mesopores from desilication. The hierarchical pore architecture is beneficial for rapid diffusion of hydrocracked products, suppressing secondary hydrocracking. An overview of design methodologies of such hierarchical zeolites is available,[50] including the definition of a hierarchy factor,[51] and its application to 10-ring pore topologies[52] and even to hydrophilic high-alumina zeolites.[53]

Combining zeolite synthesis/modification strategies for design of biomass conversion catalysts

Remarkably, assemblies of mesoporous zeolite X nanosheets can be obtained by hydrothermal templated synthesis, containing micro-, meso-, and macroporosity levels hierarchically connected in the particles.[53] Hydrophillic hierarchical zeolites show enhanced sorption affinity for polar oxygenated biomass components, stability being achieved after exchange with trivalent ions.[54] They seem suited for hydrolysis and interesterification reactions of triglycerides from microalgae or non-edible oils.

Introduction of mesoporosity in the ZSM-5 framework can also be made by direct synthesis with a hard and soft carbon template, the resulting catalysts showing good cracking activity,[55] yielding enhanced low olefins and coke content.[56] The approach converts H-ZSM-5 into an USY-type cracking catalyst. Hydrocracking catalysts based on H-ZSM-5 nanosheets[57] combine typical selectivity with enhanced mass transfer. This is now proven to be a general property of hierarchical zeolites.[58] Different nanosized zeolite topologies are also exhibiting enhanced lifetimes as refining catalysts.[59]

Given the high affinity of enzymes for converting specific biomass fractions, the combination of biocatalysis and chemical processing can be included in a conceptual biorefinery (Figure 2). The novel methodologies for tailoring zeolite porosities could unlock the full potential of zeolites for supporting enzymes, as nowadays, mesoporous silica are heavily targeted for this purpose.[60]

An important hurdle might be zeolite stability in hot liquid water of about 150–190 °C, conditions of certain biomass conversion routes. Whereas H-ZSM-5 is stable, H-USY is amorphisized increasingly faster with higher lattice Si/Al ratio of the zeolite.[61] The amorphous phase still retains Al^{IV}, though micropore volume and concentration of accessible sites is reduced. Fortunately, zeolites synthesized in F^- medium, yield intraporous polar active sites embedded in a defect-free and apolar wall.[62] Although this was proven only for Sn and Ti substitution, it could hold for Al as well. Alternatively, organosilane treatment of H-USY zeolites allows stable liquid phase catalysis at 200 °C in oil/water mixtures.[63]

Conclusions

It has been illustrated that the refinery success of a few zeolite catalysts, based on specific selectivity in mono- and bifunctional acid catalysis, can continue with biomass feeds in integrated biorefineries. Strategies adapting zeolite properties to the specificity of biomass, mainly aiming at retaining catalytic specificities under conditions of enhanced site accessibility, are now available. They involve combinations of zeolite dealumination and desilication, allowing hierarchically connecting micro-, meso-, and macroporosity in catalyst particles. The recent conceptual advances in material design and synthesis, could be at the basis of re-design and re-engineering of zeolite-based catalysts not only in petro- but also in biorefineries. The hurdle of possible zeolite instability in hot liquid water, required for such chemical conversion methodologies, is not insurmountable.

Although detailed insight in all aspects of the catalytic chemistry requires further work, attempts of shaping and forming the new generation of zeolite catalysts for use in a specific reactor environment should be addressed as well. Although out of scope of this Essay, the authors realize that zeolite-based (shape-)selective reactions in petrochemistry can be inspiring for selective transformation of biobased platform molecules.

M.D. acknowledges FWO Vlaanderen (Research Foundation – Flanders) for a post-doctoral fellowship. As support of general

statements, often use is made of selected recent reviews rather than exhaustive reference to relevant studies.

Received: January 27, 2014
Revised: April 3, 2014
Published online: July 25, 2014

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