



## Review

# Opportunities for zeolites in biomass upgrading—Lessons from the refining and petrochemical industry



David Kubička\*, Oleg Kikhtyanin

Research Institute of Inorganic Chemistry, UniCRE-RENTECH, Areál Chempark Záluží, 436 70 Litvínov, Czech Republic

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## ABSTRACT

New technologies ensuring the production of valuable products from renewable raw materials would greatly benefit our society by satisfying the ever-growing needs while reducing environmentally harmful waste and emissions. The present paper reviews the possibilities of microporous and mesoporous materials as catalysts in conversion of biomass-derived raw materials. Proven industrial applications from the refining and petrochemical sector are used as the basis for discussing the potential of new renewable-raw-materials-based processes. The examples of different studies on the applicability of zeolites as catalysts in processes requiring splitting or formation of carbon–carbon bond, isomerization, deoxygenation (including dehydration), etc. are given. The perspectives of the application of zeolites for the valorization of biomass are evaluated and several challenges are generalized, aiming at a better understanding of the relationship between physical and chemical properties of microporous materials and their behavior in the transformation of biomass-derived feedstocks.

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## Contents

1. Introduction .....	10
2. Key properties of zeolites and molecular sieves .....	11
3. Case studies .....	12
3.1. Catalytic cracking .....	13
3.2. Hydrocracking/hydroisomerization .....	15
3.3. Fine chemicals synthesis—condensation reactions .....	17
3.4. Partial de-functionalization of sugars—platform chemicals by dehydration .....	19
4. Conclusions and outlook .....	20
Acknowledgments .....	21
References .....	21

## 1. Introduction

Zeolites possess an array of unique properties that turned them into a crucial class of industrial adsorbents and heterogeneous catalysts [1,2]. Apart from their widespread use in various adsorption and separation applications, such as desiccants [3], air separation [4] or separation of iso-paraffins from *n*-paraffins [5], they revolutionized the refining and petrochemical industry by

enhancing significantly the raw material efficiency and increasing dramatically the environmental acceptability of these large-scale industrial processes.

The industrial success of zeolites has inspired intensive investigations leading to discovery of new structures and to better understanding of their functionalities and the relations between synthesis and zeolite properties [6–8], on the one hand, and between zeolite properties and their catalytic performance, on the other hand. As a result, more than 200 structures have been described up to date and new synthesis strategies have been demonstrated, including 2D zeolites, hierarchical zeolites to name a few [9–12], expanding the zeolite base to an unprecedented

\* Corresponding author. Tel.: +420 476163735; fax: +420 475 212 079.  
E-mail address: [david.kubicka@vuanch.cz](mailto:david.kubicka@vuanch.cz) (D. Kubička).

magnitude [13,14]. Despite the enormous effort, the number of industrially applied zeolites remains limited to a handful of structures [15,16].

The first milestone, i.e. development of the fluid catalytic cracking (FCC) process relying on the use of zeolites to convert extensively the atmospheric crude oil distillation residue to automotive fuel components, contributed to and at that time unimaginable growth in transport that continues to current days. It was followed by severe negative impact of the expanding industrial activities on the environment and thus life quality on the Earth. The increased public awareness resulted in strong demand for environmentally friendly processes, the second milestone, and zeolites made it possible by replacing homogeneous catalysts used for alkylation reactions and increasing the raw material efficiency, improving the product quality and facilitating separation processes.

In the recent years, the issue of the vast dependence on fossil resources including their sustainability and the related carbon dioxide emissions has become the focal concern of our time. As biomass is the only renewable source of carbon (apart from CO<sub>2</sub>), its sustainable utilization is crucial for addressing the current challenge of replacing to the maximum possible extent the fossil resources used by the chemical industry by renewable ones. While in the energy sector and to a limited extent also in the transportation sector renewable electricity sources, e.g. solar or wind energy, can be employed, most of the chemical industry and transportation fuels production have to rely on biomass utilization. Taking into account the historical developments in petroleum processing, it can be anticipated that zeolites, or more generally molecular sieves, have the potential to play “the game-changing role” once again [17].

The goal of this paper is to identify the opportunities and challenges for application of zeolites in transformation of biomass and biomass-derived feedstocks. Due to the vast possibilities and many review papers as well as a high number of particular studies devoted to biomass transformations, we have decided to approach the topic from a yet different perspective. The paper will discuss at first briefly the key properties of zeolites that made their widespread use possible and connect them to particular examples of industrial processes. Once the link between properties of zeolites and industrial processes is established, relevant case studies will be described/analyzed focusing on the analogy between the petrochemical processes and possible biomass transformation routes. The case studies will reflect the applicability of zeolites to processes requiring carbon–carbon bond splitting, formation or rearrangement, i.e. cracking, alkylation or skeletal isomerization, respectively, as well as to processes relying on functionalization or defunctionalization that include, for instance, oxidation, esterification or deoxygenation (including dehydration), respectively. Finally, the particular opportunities and challenges will be generalized to provide a broader perspective of the application of zeolites for valorization of biomass and its possible impact on the chemical industry.

## 2. Key properties of zeolites and molecular sieves

The vast variety of synthesis routes and post-synthesis modifications applicable to zeolites and molecular sieves, in general, is the key to creation of catalytic materials with an enormous variety in their properties encompassing structural, textural, chemical and acido-basic properties. The possibility to tune up zeolite properties so that they match the needs of the chemical transformations is at the heart of their industrial success.

Zeolites can be described as microporous crystalline aluminosilicates. The zeolite structure consists of interconnected SiO<sub>4</sub> and

[AlO<sub>4</sub>]<sup>-</sup> tetrahedra (the central atom of a tetrahedron is called a T-atom). The immense number of the tetrahedra connections leading to formation of (i) pores having different dimensions (e.g. 8-, 10- or 12-ring channels, i.e. having 8, 10 or 12 T-atoms in the ring defining the pore), (ii) intersecting pores and thus 1D, 2D or 3D pore architecture and (iii) cavities is the origin of the wide variety of structures (>200) known today. The synthesis of a particular structure is determined by the specific synthesis conditions (synthesis gel composition, pH, temperature, etc.) and, in some cases, the use of structure directing agents. The stability of the zeolite crystalline structures limits the size (diameter) of the zeolite channels (pores) to less than 1 nm (14-ring channels). As a consequence of their ordered microporous structure, zeolites have relatively large specific surface areas, typically in the range 300–800 m<sup>2</sup>/g. It follows that they can accommodate large number of molecules on their surface provided these molecules can penetrate the zeolite porous structure. Moreover, the basic structural characteristics of zeolites provide them with two salient features—shape selectivity and acidity—that widely determine their practical application.

The commensurable size of the zeolite channels and raw materials, reaction intermediates and/or products is the origin of shape selectivity of zeolites. There are commonly distinguished three basic scenarios—(i) smaller reactants can reach the active sites inside zeolites pores and be transformed while the larger ones cannot (reactant shape selectivity), (ii) smaller products can be formed and diffuse out of the pores while the larger ones are either not formed or diffuse very slowly and are converted before they can leave the pores (product shape selectivity) and (iii) due to the sterical restrictions inside zeolite pores some transition states can be formed while others cannot and thus only the former products can be produced (transition-state shape selectivity). The size of biomass related feedstocks will often be of the same order of magnitude as the size of zeolite channels and thus it has to be anticipated that shape selectivity and diffusion will play an important role.

The difference in valence of the T atoms—silicon is tetravalent while aluminum only trivalent—introduces a negative charge to the zeolite framework that needs to be compensated by a cation. The cation is exchangeable, i.e. this is the origin of the ion-exchange properties of zeolites that makes it possible to introduce various functionalities to the framework. Alkali metals provide the zeolite with basic properties, while their replacement with protons introduces Brønsted acidity to zeolites. Moreover, the ion exchange can be used to introduce metal cations (e.g. Cu or Pt) that after reduction will afford a bifunctional catalyst possessing an acidic function (the proton) and a hydrogenation component (the metal). Obviously, the acido-basic character of zeolites is closely related to their chemical composition, i.e. the more framework Al atoms the higher concentration of Brønsted acid sites. Traditionally, zeolites can be depending on their structure synthesized in a wide range of Si/Al ratios, i.e. in a wide range of concentration of acid sites. It has also to be noted that not all aluminum atoms are typically incorporated in the zeolite structures and the so-called extra-framework aluminum (EFAL) species are present that introduce Lewis acidity in zeolites.

Unlike mineral acids that have well-defined uniform acidity, the strength of the acid sites in zeolites is determined by the local environment in zeolites, i.e. on the type of T atom, its concentration, local geometry (e.g. Si–O–T angle) and the distribution of the T atom in the framework [18,19]. For instance, the strength of Brønsted acid sites is the highest when the next nearest T atoms to the Al T-atom are Si atoms [20]. The presence of EFAL in the vicinity of Brønsted acid sites also affects the strength of these sites [21]. Besides the adjustment of Si/Al ratio during the synthesis, various post-synthesis treatments, particularly dealumination by steaming or acid leaching, are often used to either adjust the Si/Al ratio outside the range attainable by direct synthesis or to remove EFAL to

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