



Review

Zeolite catalysts in upgrading of bioethanol to fuels range hydrocarbons: A review

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ARTICLE INFO

Article history:

Received 2 April 2015

Received in revised form 24 July 2015

Accepted 25 July 2015

Available online 1 August 2015

Keywords:

Bioethanol

Fuel-range hydrocarbons

Zeolites

Parameters

Yield

ABSTRACT

The re-ignited trend of global bioethanol production indicated that new valorization paths are necessary. Bioethanol upgrading into fuel range hydrocarbons (FRH) via catalytic dehydration represents an alternative for handling the challenges associated with the blending options. The paper carefully examined the recent literature on the role of zeolite catalysts during the reaction. Effects of parameters like catalyst topology and textural properties, modification with metals, acidity and reaction conditions in enhancing the yield of FRH were critically examined. The influence of these parameters on the reaction mechanism was also simultaneously discussed. The paper finally presented an outlook on new research paths.

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Contents

Introduction	1
Ethanol to hydrocarbons (ETH) over zeolites	2
Role of zeolite topology and textural properties	3
Role of metal modification	5
Role of zeolite acidity	7
Role of reaction conditions	9
An outlook	11
Conclusions	12
Acknowledgements	12
References	12

Introduction

The global reliance on fossil fuels as sources of energy and chemicals is increasingly considered unsustainable subject to the associated challenges. The fossil fuels are unevenly distributed and are particularly non-renewable [1–3]. Their continuous production and utilization are associated with serious environmental

consequences such as destruction to aquatic species due to oil spillage [4,5], global warming due to the emission of greenhouse gases like CO₂ and CH₄, consequent reduction in fertile agricultural land and the declining of freshwater for household and industrial applications [6–8]. A shift to the renewable alternatives is currently considered as one of the possible viable options for addressing the problems [9–11]. For this reason, ethanol (i.e. bioethanol) production from biomass-based feedstock and upgrading into fuels and chemicals is becoming an issue of special interest globally [12–14]. In the USA, both the number of ethanol production plants and the level of production have been increasing since 1990s. By the year 1999, there were only 50 ethanol production plants but the figure increased to 81, 189 and

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211 production plants in 2005, 2010 and 2013, respectively [15]. Similarly, in 1999, the annual USA ethanol production was 1.47 billion gallons but risen to 3.90, 10.94 and 13.31 billion gallons in 2005, 2009 and 2013, respectively. The trend is similar in many other world regions [16]. The annual ethanol productions in China and Canada in 2009 were 541.55 and 290.59 million gallons, respectively. These respective figures however increased to 555 and 449 million gallons in 2012. In Australia and Europe, 56.80 and 733.6 million gallons were produced in 2008, respectively, but the annual production increased to 71 and 1139 million gallons in 2012. The African continent, which represents the least global ethanol producer, had an annual production of 38.31 million gallons in 2011 which increased to 42 million gallons in 2012 [16]. The total global annual production was estimated at 17,335 and 19,534 million gallons in 2008 and 2009, respectively. Fig. 1 reports the 2013 ethanol production for the global regions. USA had the highest production of 13,300 million gallons followed by Brazil with a production of 6,267 million gallons [16]. Countries in Europe and China produced 1371 and 696 million gallons, respectively. In India and Canada, the productions were 545 and 523 million gallons, respectively, whereas 727 million gallons for the rest of global countries, including those in the African continent. The total global production of the year 2013 was therefore estimated at 23,429 million gallons, an equivalent of 20% growth from 2008. The production was estimated to hit 41,740 million gallons (i.e. 158 billion liters) by the year 2023 [17].

There is no doubt the above statistical information revealed a substantial growth in the production of ethanol over the years, with good potentials to provide the global industry with abundant feedstock for fuels and chemicals production. Currently, ethanol is blended with gasoline in a ratio up to 10%, with a view to increase the fuel anti-knocking (i.e. octane) properties and reduce the emissions of regulated pollutants including CO₂, NO_x and polyaromatic hydrocarbons. In the USA more than 95% of the gasoline used in automobiles is blended with 10% of fuel-grade ethanol. Similarly, the Environmental Protection Agency (EPA) permitted the blending of 15% ethanol with 85% gasoline for used in new vehicles (i.e. 2001 and beyond models) [18]. Different countries of the world are employing between 5 and 10% and higher ethanol blends with gasoline as transportation fuels [19–21]. However, the blending of ethanol for used as transportation fuels has some incompatible challenges that include destruction to vehicle engines [22–24]. Conventional automobile engines are usually constructed with components that brittle with time. These components consequently disintegrate in the presence of alcohol, clogging the engine with sludge and triggering engine seizure [25]. Configuration into modern engines with 100%

compatible ethanol blend properties will involve serious cost implications and can be considered difficult, especially for the low-income nations. As an excellent solvent, ethanol can dissolve resins in engines, causing complications including clogged injectors. Its ability to absorb water can also cause phase separation in engines. Similarly, application of ethanol blends in marine and aviation engines can be considered very difficult due to poor cold flow properties [25].

An important alternative to the blending option recently considered is the upgrading of ethanol into fuels (e.g. gasoline and diesel) range hydrocarbons, with properties similar to the original fuel compositions. Ethanol can be converted into paraffins (both n- and i-), olefins and aromatics using solid acid catalysts like zeolites and heteropoly acids [26–30]. The paper therefore reviewed recent literature on the role of zeolite catalysts for the ethanol to hydrocarbons reaction. Emphasis was given to the role of zeolite topology, textural properties, acidity and reaction conditions in improving the yield of fuels range hydrocarbons. These parameters are very influential for reactions involving the zeolite catalysts [31–34].

Ethanol to hydrocarbons (ETH) over zeolites

The catalytic upgrading of ethanol into hydrocarbons was during the early days centered on the use of liquid acid catalysts such as concentrated sulfuric and phosphoric acids [35,36]. This process was mainly employed for the production of ethylene via dehydration and was abandoned due to the cost and environmental challenges associated with homogeneous acid catalysis. The application of the solid acid catalysts (i.e. zeolites) is a more recent technology that also provide suitable opportunities for the production of a range of other hydrocarbons such as paraffins, aromatics and higher olefins. Mechanistically, the reaction can be achieved at two different temperature boundaries depending on the products of interest. At temperatures <300 °C, ethanol can be mainly dehydrated into ethylene whereas to paraffins, aromatics and C₃₊ olefins at temperatures ≥300 °C. However, this also depends on other factors such as zeolite acidity and topological properties.

Different reaction mechanisms have been proposed for the ETH reaction by different authors. One of these proposals involved the dehydration of ethanol into diethyl ether (DEE) as an intermediate or the direct ethanol dehydration to ethylene (Fig. 2). The ethylene subsequently undergoes further reactions like oligomerization, cracking, cyclization and aromatization to produce higher hydrocarbon compounds. According to Meeprasert et al. [37], the reaction is generally initiated by the interaction of ethanol with

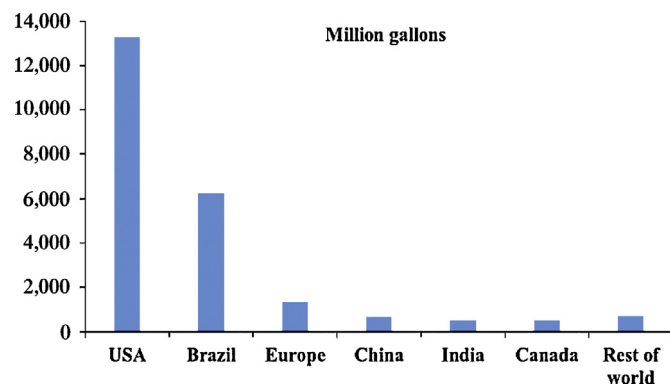


Fig. 1. Ethanol production for global regions in 2013. Data source: [16].

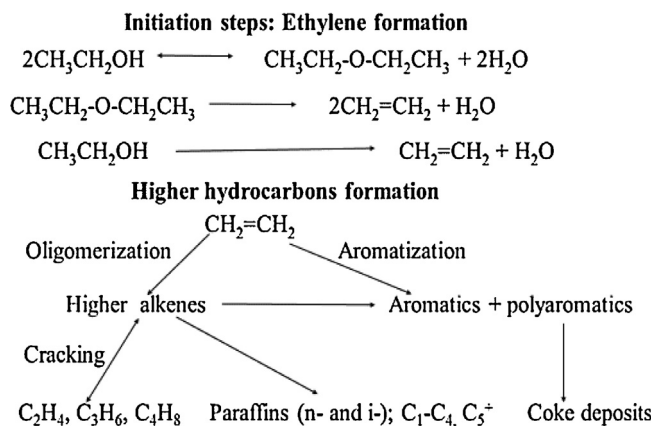


Fig. 2. Mechanism of hydrocarbons formation from ethanol.

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