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Activity of solid acid catalysts for biodiesel production: A critical review

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ABSTRACT

Homogeneous acid catalysts received wide acceptability because of their fast reaction rates. However, postproduction costs incurred from aqueous quenching, wastewater and loss of catalysts led to the search for alternatives. Until recently, heterogeneous base catalyzed-biodiesel production also gained the attention of most researchers. This was because the process minimized the problems of homogeneous catalysis in terms of catalyst regeneration and recycling in continuous processes. However, despite these advances, the ultimate aim of producing biodiesel at affordable cost is yet to be realized. Further, the process requires refined feedstocks which account for as high as 88% of the final production costs. Thus, the focus of many research efforts is towards the rational design and development of solid acid catalysts aimed at reducing biodiesel production costs. Therefore, this study reviewed current literature on the activities and advantages of solid acid catalysts used in biodiesel production. It discussed in details how the preparation method and prevailing reaction conditions affect the catalytic activity of the catalyst. The review concluded by suggesting way forward from the traditional trial-and-error method to a rational means of determining catalytic activities.

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1. Introduction

For several decades, energy crisis have being confronting the world due to the excessive utilization of the world's depleting oil reserves by the ever-increasing human population [1]. On one hand, the world's economy is largely dependent on the transportation of goods and services [2,3], while on the other hand, transportation is mainly dependent on energy from petroleum. In fact, the transportation sector is 96% dependent on fossil fuels with an annual worldwide fuel consumption of 62% [4]. This is despite other sources of energy such as coal, natural gas, hydroelectricity and nuclear power [5]. Apart from the ever-increasing prices of petroleum fuels, more worrying issues associated with utilizing these fuels include deteriorating health standards and environmental degradations. These concerns have led to the search for sustainable biofuel alternatives [6]. These researches are aimed at curbing the menace of climate changes while sustaining a stable world economy with reduced health problems. A renewable and sustainable fuel currently receiving renewed interests and intensive experimentations since the work of Rudolf Diesel is biodiesel [7–11]. It is increasingly becoming attractive as an alternative to petrodiesel. It is worthy to note that biodiesel is considered the fastest growing industry worldwide [12,13]. This is evident from the deluge of publications available from both the open and patent literature [10,13–17]. Nonetheless, the central policy of biodiesel to replace petrodiesel is yet to be achieved [18,19]. This is notwithstanding the tax reliefs and subsidies [6] the biodiesel industry enjoys from governmental agencies. Evidently, to achieve this target, certain technological advancements and sustained governmental policies are essential. These include: (1) Establishing proficient systems for producing vast quantities of feedstocks at affordable costs. (2) Developing novel catalysts with higher activities which can achieve greater yields in shorter time and lesser refining difficulties. (3) Radical innovations for separating and refining crude biodiesel. (4) Enacting new policies that will favor sustained biodiesel production. (5) Minimizing costs, energy and water usage by implementing the excellent findings from the research communities [20].

In line with these, several attempts are ongoing to improve biodiesel production processes [21]. Prominent amongst them is the prospects of solid acid catalysts for the simultaneous esterification and transesterification of feedstocks especially those containing high amounts of free fatty acids (FFAs). Report by West et al. [22] showed that solid acid-catalyzed process is more economical than supercritical processes, homogeneous acid and alkali catalysis. The study also highlighted it as having the least capital investment with the highest return on investment, while technically being a simple process. Consequently, several solid acid catalysts were developed to overcome the disadvantages of heterogeneous alkaline catalysts currently used in the industries. The challenging feat however is in attaining a breakthrough on the mechanism of fatty acids (FAs) esterification by solid acid catalysts. This is because it is more difficult to develop suitable solid acid catalysts for esterifying long-chain acids compared to the shorter acids such as acetic acids [21,23]. Accordingly, the aim of numerous recent research efforts is to develop novel solid acid catalysts. Certainly, these catalysts must be active, selective, reusable, stable and reproducible via simple economically viable procedures [24,25].

Usually, turnover frequency (TOF), strength and concentration of the catalytic sites, surface area, Brønsted/Lewis acidity and porosity (morphology) of the catalyst and its support are the variables used in describing solid acid catalysts. Manipulating these properties can lead to enhanced activity and product selectivity [26,27]. Heterogeneous catalysts are best described as "nonequilibrium" or "dynamic" catalysts. This is due to the intimate dependency of the catalytic structures on the prevailing reaction conditions. Small changes in the reaction medium may result in large or complete morphological changes on the catalyst surface structure because of the adsorbate-induced surface–reconstruction relationship. Consequently, the assertion that the active state of a solid acid catalyst is solely predominant during the catalytic process becomes plausible. Hence, the usual assumption that the state and number of active sites remain constant under varying reacting conditions becomes inadequate [28]. It is pertinent therefore for researchers to decipher the optimal factors regarding the adsorbate-induced surface–reconstruction relationship that will lead to better activities. The aim of this article therefore, is to discuss the need for advances on solid acid catalysis as ways of ensuring biodiesel commercialization against petrodiesel. To achieve this aim, the article reviewed the factors that affect catalytic activity and stable acidic sites. This review consists of six sections; the introductory section and general discussion on issues regarding heterogeneous base and homogeneous acid catalysts in section two. The different types of solid acid catalysts are reviewed in section three. Instances that discussed their strengths and weaknesses were presented briefly to stimulate further researches. Section 4 on the other hand contains in-depth analyses of activities of the catalysts while section 5 gives the current scenario, future challenges and prospects of solid acid catalysis. The discussion concluded by proffering possible solutions that will ensure the prominence of solid acid catalysts in biodiesel production.

2. Issues with heterogeneous base and homogeneous acid catalysts

Legislations aimed at reducing vehicular particulate emissions and the high prices of fossil fuels favor biodiesel production [16,23,29,30]. However, the high cost of feedstock accounts for ca. 88% total biodiesel production costs. This hinders the economic competitiveness of biodiesel with respect to petrodiesel [31,32]. Low quality feedstocks such as nonedible oils, used cooking oils [16,33,34] and microalgal oil which are affordable and readily available serve as means of reducing biodiesel production costs [18,35]. Nonetheless, transesterifying such inexpensive feedstocks with homogeneous acid catalysts; though not susceptible to high FFA contents, requires expensive equipment. Other challenges faced by this technique include high temperature requirement, product separation and purification, and nonreusability of the catalysts [36]. Similarly, due to the presence of water and FFAs, the use of conventional alkaline catalysts faces saponification and separation challenges. The reaction between the FFAs and alkali catalysts produces soaps such as sodium or potassium oleate and water. At ambient temperatures these soaps solidify into undesired gel and semi-solid mass. In addition, hydrolysis of the triglycerides with water produces new fatty acid and diglycerides. Therefore, the transesterification reactions require anhydrous alcohol and refined feedstocks [37] which contain FFAs as low as 0.5% w/w [17,32,38]. Pretreating the inexpensive feedstocks becomes necessary before the transesterification process [6]. Sulfuric acid and methanol (at 400 kPa and 70 °C) are used to reduce the FFAs to negligible values. However, special units for water and methanol recovery and sulfuric acid neutralization are required for these postproduction processes. These requirements account for as high as 75% of the final production costs. Leaching of the alkaline catalysts into the reacting medium has also been a major concern. Moreover, it is still not clear whether the activity of the alkaline-catalyzed reaction is because of the leached catalysts which homogenizes into the liquid phase [35].