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Highly stable gasified straw slag as a novel solid base catalyst for the effective synthesis of biodiesel: Characteristics and performance

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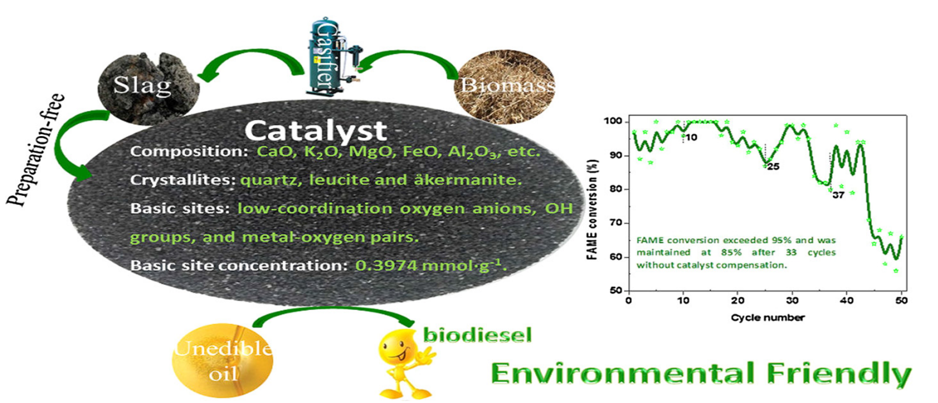
HIGHLIGHTS

- A preparation-free gasified-straw slag as solid base catalyst for biodiesel production.
- The catalyst shows superior stability and activity in 33-run test.
- Three crystallites, quartz, åkermanite, and leucite are included in the catalyst.
- Fixed-crystal-structure was responsible for the excellent stability.
- Basic sites include low-coordination oxygen anions, OH groups, and metal-oxygen pairs.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel solid base catalyst derived from gasified straw slag for producing biodiesel was prepared by simple pulverization and sieving. This catalyst exhibited high stability, low leaching of the catalytic species, and good catalytic activity, caused by high-temperature melting in the biomass gasifier. SiO_2, CaO, K_2O, MgO, FeO, and Al_2O_3 were the common constituents (calculated as oxides) as per XRF analysis and EA. XRD and TEM-EDS analysis indicated that the catalyst comprises three crystallites: quartz, leucite, and åkermanite. The catalyst was strongly basic with a basic site concentration of 0.3974 mmol·g^{-1}, including strongly basic low-coordination oxygen anions, moderately basic OH groups, and metal–oxygen pairs, as identified by CO_2-TPD and IR. TGA results indicated that the catalyst is thermally stable up to 400 °C, which is greater than the typical reaction temperature. BET analysis results indicated that the slag exhibits a broad pore distribution with pore diameters of 5–15 and 45–75 nm. The catalyst exhibited high catalytic activity and stability, exhibiting a fatty acid methyl ester (FAME) conversion of 95% for transesterification conducted at 200 °C for 8 h with a catalyst dose of 20% and a methanol–oil molar ratio of 12:1. The FAME conversion remained greater than 85% even after reusing the catalyst for 33 reactions without any appreciable loss of catalytic activity. Small amounts of K and Mg (<10 ppm) leached into the product from the catalyst. These results indicated that the gasified straw slag catalyst demonstrates promise for producing biodiesel.

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1. Introduction

Currently, the world is facing two serious problems: environmental pollution and energy consumption. With the combination of dwindling fossil fuels and natural resource reserves and growing concerns over climate change caused by carbon dioxide emissions, the development of clean, sustainable energy supplies is urgently required [1–3]. One promising approach to alleviate energy problems involves the use of biomass energies, e.g. biodiesel and biofuel, as abundant, diverse, and environment-friendly energy sources [4–6]. Biodiesel has attracted considerable interest as sustainable fuels because of its low sulfur content, low hydrocarbon aroma, high cetane number, high flash point, and low environmental impact [7–10].

Biodiesel is a mixture of long-chain fatty acid methyl esters (FAME) produced from the transesterification of triglycerides, derived from vegetable oils or animal fats, with methanol [11–13]. Typically, the commercial production of biodiesel involves the use of strongly basic solutions (i.e. NaOH, KOH, and KOMe) as catalysts [14–16]. However, such homogeneous base catalysts cannot be recycled after reaction completion, and their separation from the produced biodiesel requires washing with copious amounts of water, leading to large amounts of wastewater, as well as equipment corrosion, high energy accumulation, and operation costs [10,17–19]. On the contrary, the use of a solid base catalyst facilitates a more ecologically friendly synthetic route [20–22].

Various solid bases have been reported, e.g. metal oxides, such as CaO [23] and TiO_2 [24]; mixed oxides, such as CaO/MgO [25] and CaO/CeO_2 [26]; alkali or alkaline earth oxides on MgO/SiO_2 supports [27]; alkali-doped metal oxides, such as Li/CaO [28]; zeolites [29,30]; and hydrotalcites [31]. Calcium-based solid base catalysts have attracted significant attention for the production of biodiesel because of their high basicity, mild catalytic conditions, and low preparation costs. However, the severe leaching of calcium species into the solution is observed even under mild conditions, leading to only a few cycles of catalyst reuse [32,33].

Recently, alternative catalysts derived from renewable biomass and industrial waste materials are attracting attention [34]. Biont shell catalysts produced from incompletely carbonized natural products, e.g. shells from eggs [35], oysters [36], mussels [37], crabs [38], turtles [11], and shrimp [39], as well as catalysts derived from industrial wastes, e.g. carbide slag [40], blast furnace slag [41], fly ash [42], and aluminium dross [43], have been reported for producing biodiesel. In addition, these catalysts have been prepared by multistep processes, which involved the loading of active components and activation of the catalyst because biomass and wastes only serve as catalyst carriers. Regarding the aforesaid solid base catalysts, the main catalytic species of the catalysts is calcium; accordingly, the same problem is observed with the use of CaO-based catalysts. Furthermore, these solid base catalysts are utilized as powders, leading to significant difficulty in catalyst reusability, as well as separation from biodiesel products. More importantly, these solid base catalysts exhibit low activities. Thus, the development of an ideal heterogeneous catalyst for producing biodiesel, which is eco-friendly, economical, and stable, as well as exhibits high catalytic activity, is a significant challenge.

To address these issues, a novel gasified straw slag catalyst was developed. As gasified straw slag was the by-product from biomass gasification in biomass gasifiers, e.g. (circulating) fluidized-bed gasifiers and updraft or downdraft gasifiers, it does not incur any cost or is marginal. Because of a significantly high temperature of greater than 900 °C at the bottom of biomass gasifiers, after long-period operation, in the presence of ash, base-metal-contained biomass melts at the bottom of gasifiers, forming slag [44,45]. Generally, biomass residues can be classified into three categories: straw, husk, and wood powder. For the same type of biomass, the gasifier slag exhibits a similar chemical composition (expressed as oxide), i.e. CaO, MgO, K_2O, and Na_2O. These oxides contain significantly strong active sites for transesterification, demonstrating promise for the highly effective production of biodiesel.

Hence, in this study, catalysts obtained from gasified straw slag were directly used after a facile grinding. Catalytic performance was assessed by the transesterification of rapeseed oil with methanol. Effects of reaction temperature, methanol–oil molar ratio, catalyst concentration, and reaction time on transesterification were investigated. A combination-characterization method of utilizing TEM, XRD, TPD, etc., was employed, from which, the complex compositions of the slag, crystal structure, as well as the basic characteristics or basicity were well-resolved. This catalyst exhibited advantages of good stability (recycled 50 times), strong endurance to corrosion, significantly low leaching of catalytic species, high catalytic activity, and nearly free of cost. Such superior stability was determined to be related to the catalyst crystal structure. The disclosure of high-stability crystallite paves a route for tackling the bottlenecks associated with the research and development of solid base catalysts.

2. Experimental

2.1. Materials

Rapeseed oil was purchased from the market. Methanol and n-hexane were purchased from Tianjin Damao Chemical Co. and Tianjin Fuyu fine Chemical Co, respectively. The GC grade (>99.0%) methyl ester standards, which include methyl myristate, hexadecanoic acid methyl ester, methyl cis-9-octadecenoate, methyl linoleate, methyl linolenate, methyl cis-11-eicosenoate, and methyl cis-13-docosenoate were obtained from Sigma-Aldrich.

2.2. Catalyst preparation

Catalysts were derived from gasified straw slag, prepared by a simple procedure involving pulverization and sieving to obtain 40–60 mesh particles, and stored in a vacuum desiccator until use. The slag in this study was produced during straw gasification in a gasifier. Table 1 summarizes the operation conditions of the gasifier.

2.3. Catalyst characterization

The elemental composition of the catalysts was analysed by wavelength-dispersive X-ray fluorescence (XRF) and elemental analysis (EA). The crystal structure was identified by powder X-ray diffraction (XRD) using a PANalytical X'Pert PRO MPD diffractometer. Thermogravimetric analysis (TGA) was performed on a TGA Q50 V20.13 Build 39 instrument from 40 °C to 1000 °C at a ramping rate of 10 $°C·min^{-1}$ under a flow of N_2 of 30 $mL·min^{-1}$ using α-Al_2O_3 as the standard. N_2 sorption measurements were performed on an automatic specific surface and pore size analyser

Table 1
Gasifier operation conditions.

Parameters	Value	Parameters	Value
Feedstock	Straw	Temperature in the oxygenation area	Over 900 °C
Gasifier type	Fluidized-bed	Equivalence ratio	0.25
Gasification agent	Air		