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Function promotion of $SO_4^{2-}/Al_2O_3{-}SnO_2$ catalyst for biodiesel production from sewage sludge

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Catalysts are critical materials for biodiesel production using sewage sludge feedstock. In this research, different $SO_4^{2-}/Al_2O_3{-}SnO_2$ catalysts were prepared and characterized. The catalysts prepared at different conditions were characterized through Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), NH_3-temperature-programmed desorption (NH_3-TPD), NH_3 adsorption FT-IR, and TGA. Then, esterification/transesterification reaction was performed with the lipid extracted from sewage sludge to verify the activity of these catalysts. Results showed that the catalysts with n(Al):n(Sn) = 1:10 prepared by 79 wt% H_2SO_4 possessed the best physical properties with a large number of active catalytic sites, which led to the biodiesel yield of 73.3% (based on dried extracted crude fat) under the optimized reaction conditions at 130 °C as reaction temperature, 0.8 g as catalyst loading for lipids extracted from 10 g freeze-dried sludge, 4 h as reaction time. Catalysts characterization results showed that acidity, acid sites and Al/Sn molar ratio play an important role in the activity of catalysts. The thermal properties showed that 450 °C was the suitable calcination temperature for catalyst preparation. The optimized $SO_4^{2-}/Al_2O_3{-}SnO_2$ catalyst in this research will have a bright future in the field of sludge production of biodiesel.

1. Introduction

As the by-product of wastewater treatment plant (WWTP), sewage sludge has once been ignored and has not been environmentally treated. However, with the increase disposal rate of wastewater, the amount of sewage sludge rapidly grew up [1–3]. Sewage sludge from WWTP normally contains about 80% water, considerable organic compounds, pathogenic bacteria, some heavy metals, persistent organic compounds, etc [4,5]. There are many technologies which can treat sewage sludge with merits and shortcomings [6–9]. This research would like to talk about recycling sewage sludge as one of the source for biodiesel.

As a sustainable and green fuel, biodiesel has gained increasing attention. Considering the environmental ethics and cost, the raw material for biodiesel production has changed from normal biomass to organic waste [10–12]. Sewage sludge contains relatively high concentration of lipid (>10%) [13] and has no or negative cost of acquirement and abundant with a steady stream. The lipids can be extracted from sewage sludge and then be transferred into biodiesel by esterification and transesterification with the function of catalyst [10,14]. Our previous research found that the lipids in sewage sludge contain more than 14 big category of cellular lipids, >30 kinds of fatty acid, wax, and so on [13]. Lipids in sewage sludge has complicated origin and contains not only glyceride and fatty acid, which were the classic reactant for esterification/transesterification, but also considerable ceramide, coenzyme, phosphatidylcholine, phosphatidylethanolamine (PE), phosphatidy linositol (PI), cardiolipin (CL) and so on [15,16], which have seldomly been reported to be the reactant of esterification and transesterification. As catalysts play a very important role in the esterification and transesterification reaction, many scholars have focused their research on the development of high-efficiency catalysts in the field of biodiesel production from sludge sewage. Some related studies have confirmed that H_2SO_4 is an excellent catalyst [10], Qi et al. [17] of our research group used concentrated H_2SO_4 to obtain 16.6% (based on total dry weight of activated sludge) yield of biodiesel from A2/O sludge, and the purity of FAMEs was 96.7%.

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Although H_2SO_4 exhibits good function, it can't be recovered and have to be neutralized, thereby increasing the cost [15,18]. Alkaline catalysts have been successfully applied in biomass-originated oil/lipids (such as palm oil, rapeseed oil, etc.) in esterification/transesterification reaction, but they have less function in sewage sludge-originated lipids [19–22]. Our previous research tested the traditional alkaline solid catalysts such as KOH, solid KOH/activated carbon (KOH/AC) and KOH/CaO [18], the maximum yields of biodiesel were only 1.2%, 6.8% and 6.0% (based on total dry weight of activated sludge), respectively. According to our previous experimental data, the yield of biodiesel obtained by anion exchange resin as catalyst was only 8.1%. As a result, this research started to look for suitable catalysts in solid acid catalysts.

Solid acid catalysts generally refer to the carrier materials that can load various acids. They can be broadly classified as supported solid acids, solid super acids, metal oxides and composites, cation exchange resins, and zeolite molecular sieves. These catalysts have several advantages, such as high stability, strong acidity, easy recycling, low corrosion, and simple product separation [23–26]. SiO_2, Al_2O_3, ZrO_2, SBA-15, and attapulgite are catalyst carriers that are commonly used due to their relatively large specific surface area and high catalytic efficiency [8,27–29].

Table 1 summarizes the catalyst function of different solid acid catalysts for biodiesel production with vegetable oil or animal fat feedstocks. It is reported that some sulfated metal oxides produce super acid materials with surface acidity and much larger surface areas than those of metal oxides without sulfate [48]. Table 1 also reveals that solid acid catalyst with SO_4^{2-} normally performs better functions. In 1979, Hino and Arata [49] first synthesized SO_4^{2-}/M_xO_y-type (M = Zr, Fe, Ti, etc.) solid super acids, which show remarkable catalytic performances in the isomerization of alkanes. Since then, these solid super acids receive considerable amount of attention [48].

SO_4^{2-}/SnO_2 is one kind of SO_4^{2-}/M_xO_y solid super acid, which has the highest acid strength; it also exhibits superior catalytic performance in various reactions [50]. It's reported that the introduction of Al can stabilize the S species on the catalyst surface, increase the acidity of the catalysts, and improve the catalytic activity of the SO_4^{2-}/M_xO_y solid super acid [51,52]. However, studies on $SO_4^{2-}/Al_2O_3-SnO_2$ catalysts used for the esterification/transesterification of lipids extracted from sewage sludge, as well as their own structure and other applications, are lacking. This research mainly investigates the freeze-dried sludge obtained from the A2/O process in Beijing to produce biodiesel via $SO_4^{2-}/Al_2O_3-SnO_2$ solid acid catalysts. One purpose of this research is to optimize the preparation condition of the $SO_4^{2-}/Al_2O_3-SnO_2$ by adjusting the SO_4^{2-} loading and the Al/Sn molar ratio, which are the most important factors to influence the performance of that catalyst. The other purpose is to optimize the reaction condition of esterification/transesterification of lipids extracted from sewage sludge with $SO_4^{2-}/Al_2O_3-SnO_2$ as catalysts such as reaction temperature, reaction time and catalyst loading.

2. Materials and methods

2.1. Materials

The sewage sludge samples were collected from a typical big scale WWTP that had undergone A2/O process in Beijing, China. These samples are the mixed sludge of primary sedimentation and excess sludges. The basic characteristics of sewage sludges are shown in Table 2.

2.2. Catalyst preparation and characterization

2.2.1. Catalyst preparation

$SO_4^{2-}/Al_2O_3-SnO_2$ catalysts were prepared via a coprecipitation method. $SnCl_4 \cdot 5H_2O$ and $Al_2(SO_4)_3$ were dissolved in 600 ml of deionized water with n(Al):n(Sn) = 1:5, 1:10, 1:15. Then, 30% $NH_3 \cdot H_2O$ was added to the beaker under room temperature until the solution pH adjusted 8.0 in a fume hood. The liquid mixture was gradually changed to suspended state. After filtration, the separated precipitates were suspended in 4 wt% of CH_3COONH_4 solution and stirred for 1 h. After secondary filtration, the precipitates were

Table 2
The basic characteristics of sewage sludge.

Components	Sewage sludge
Moisture content(%)	83.0 ± 0.5
VS(%)	65.3 ± 0.6
Crude fat * (%)	16.1 ± 0.1
Crude protein * (%)	26.2 ± 8.2
TOC(%)	32.7 ± 0.2

Table 1
Results of biodiesel production by solid acid catalysts.

Catalyst	Raw material	Reaction conditions	Yield(%)	References
H-type faujasite zeolite	Soybean	5:1,0.5 wt%,60 °C,1 h	75	[30]
Modernite zeolite	Soybean	5:1,0.5 wt%,60 °C,1 h	80	[30]
$H_3PW_{12}O_{40}/SiO_2$	Palm fatty acid distillate	12:1,15 wt%,85 °C,15 h	96.7	[31]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Sesame oil	40:1,3 wt%,260 °C,1 h	92	[32]
WO_3-ZrO_2	unspecified	19.4:1, 75 °C,20 h	85	[33]
$ZrO_2-Al_2O_3$	Jatropha	9:1,7.61 wt%,150 °C,4 h	90.32	[34]
$Al_2O_3/TiO_2/ZnO$	Rapeseed oil	5 wt%,200 °C,8 h	93.7	[35]
Ar-SBA-15	Palm oil	20:1,6 wt%,140 °C,2 h	90	[36]
Anion/cation exchanged resin	Glycerides	10:1,4 wt%,50 °C,4 h	98.8	[37]
$SiO_2-SO_3H/COFe_2O_4$	Rambutan tree oil	20:1,5 wt%,65 °C,5 h	95	[38]
$AlCl_3 \cdot 6H_2O$	Brown grease	10:1,2 wt%,42 °C,<4 h	90	[26]
SO_4^{2-}/ZrO_2	Sea Lime Tree	8:1,6 wt%,180 °C,3 h	84	[39]
	Palm oil	8:1,8 wt%,60 °C,2 h	82.8	[40]
	Mango oil	12:1,8 wt%,150 °C,3 h	94.1	[40]
	Lauric acid	3:1,3 wt%,180 °C,1 h	96	[41]
SO_4^{2-}/SnO_2-SiO_2	Jatropha	15:1,3 wt%,180 °C,2 h	97	[42]
	Moringa	5:1,3 wt%,150 °C,2.5 h	84	[43]
	Large fruit croton	15:1,3 wt%,180 °C,2 h	95	[44]
SO_4^{2-}/TiO_2-SiO_2	Palm fatty acid distillate	5.85:1,2.97 wt%,150 °C,3.12 h	93.3	[45]
	Acidified cottonseed oil	9:1,3 wt%,200 °C,6 h	92	[46]
$SO_4^{2-}/ZrO_2-Al_2O_3$	Kitchen waste oil	1.4:1,0.3 wt%,200 °C,4 h	98.4	[47]