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Study on the preparation, characterization of a novel solid Lewis acid Al^{3+}-SO_4^{2-}/MWCNTs catalyst and its catalytic performance for the synthesis of biodiesel via esterification reaction of oleic acid and methanol

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A B S T R A C T

A novel solid Lewis acid catalyst Al^{3+}-SO_4^{2-}/MWCNTs was prepared by impregnating multi walled carbon nanotubes (MWCNTs) with concentrated sulfuric acid and Al^{3+}. The physical and chemical properties of Al^{3+}-SO_4^{2-}/MWCNTs was characterized by X-ray diffraction, transmission electron microscopy, Raman spectroscopy, X-ray fluorescence spectroscopy, NH_3 temperature programmed desorption, X-ray photoelectron spectroscopy and pyridine adsorption IR spectra. The catalytic activities of SO_4^{2-}/MWCNTs, Al^{3+}-SO_4^{2-}/MWCNTs and Al^{3+}-SO_4^{2-}/SWCNTs, Al^{3+}-SO_4^{2-}/C were compared when they were respectively applied for the catalytic synthesis of biodiesel via esterification reaction of oleic acid and methanol. Results showed that Al^{3+}-SO_4^{2-}/MWCNTs had the highest catalytic activity: the conversion ratio of oleic acid reached 95% when reaction temperature was 65 °C, mass ratio of catalyst to reactants was 0.9 wt% and molar ratio of methanol to oleic acid was 12:1 after 7 h. The high catalytic activity of Al^{3+}-SO_4^{2-}/MWCNTs can be ascribed to the flow and escape of electronic is very easily in the tubular structure of MWCNTs since it has low C1s binding energy. It will stimulate a strong interaction between Al^{3+} and SO_4^{2-}, accompanied with the formation of a stable coordination bond, which increased the crystallization degree of Al^{3+}-SO_4^{2-}/MWCNTs catalyst and improved the combination stability of SO_4^{2-} and MWCNTs. In addition, S=O band can exert strong electron induced effect, which leads to the increasing of the valence electron layer density of Al element, reduces the shielding effect of outer electrons on core electrons and increases the binding energy of core electrons. It directly affects the electronic state of S and Al and changes the chemical state of SO_4^{2-}, enhances the absorption capacity of Al^{3+} and increases the imbalance of the system. Eventually, it changed the original acidity of the Al^{3+}-SO_4^{2-}/MWCNTs catalyst and enhanced its Lewis acidity. Hence, the acid site of Al^{3+}-SO_4^{2-}/MWCNTs is mainly comprised by Lewis acid, which is favorable for the avoiding of the occurrence of hydration of Brönsted acid active sites.

1. Introduction

Biomass energy can be directly used as fuel for automobiles or other power devices, including methanol, ethanol and biodiesel. Compared to methanol and ethanol, the energy density of biodiesel is close to petrochemical diesel, biodegradable, non-toxic, no sulfur, harmless to the environment, so it can meet the health effects testing requirements of Clean Air Act Amendments of USA. Hence, biodiesel is a kind of ideal clean alternative fuel for petrochemical diesel. As a potential clean fuel, the global biodiesel production has reached 32 million 800 thousand tons in 2016, Europe accounted for about 43% of all the production of biodiesel, and the production of biodiesel in China is about 336 thousand tons [1].

Several types of vegetable oil and animal grease can be used to produce biodiesel, such as edible and non-edible vegetable oils, animal fats, algae and waste cooking oils. However, a fact cannot be ignored that the cost of raw oil nearly accounts for 50% of the total production cost of biodiesel when it was produced from a pure vegetable oil or animal grease [2–7]. Although China is a country with rich plant resources and broad distribution advantages, which can provide great convenience for the selection of raw materials of biodiesel. However, China is also a populous country, vegetable oil still needs a lot of imports and consumes as edible oil priority, which determines that China cannot use edible oils as raw material for biodiesel production. It also should be noticed that the annual consumption of edible oil is about 1600 million tons in China, resulting in a waste of 1 million 600 thousand tons of animal fats and vegetable oils due to nearly 10% of the

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edible oil was abandoned after use [8]. Therefore, if we can reasonably use waste animal fats and vegetable oils for the production of biodiesel, it can greatly reduce the production cost of biodiesel. However, the composition of the waste animal fats and vegetable oil is very complex, so it put forward a severe requirement for a catalyst that can maintain high catalytic activity and stability in the reaction process.

At present, carbon based solid acid has become a hot spot in the research of solid acid catalysts at home and abroad due to it has several advantages, such as simple preparation, strong proton acidity and high catalytic activity [9–11]. Carbon based solid acid is commonly refers to a kind of material, which was prepared from the selection of a carbon material first, and then the surface of it was modified by a liquid acid (mainly concentrated sulfuric acid). At present, research related with the preparation of carbon based solid acid and application of them in the catalytic synthesis of biodiesel was reported every year, but focus primarily on the selection of different carbon material, different acid modification group and different preparation method how to influence the structural differences (such as pore size, crystallinity and dispersion, etc) of the obtained carbon based catalyst, and eventually how to affect its catalytic performance. However, few studies have been reported what impact will occur to the surface acidity and stability of carbon based solid acid catalyst when the carbon based materials was modified by liquid acid with the introduction of some metal or non metal ions at the same time. Due to the carbon based solid acid is usually constitutes by proton acid active sites (Brönsted acid site), most belong to the sulfate type carbon based solid acid, so the hydrophilicity of the catalyst will be furtherly improved after a large number of hydrophilic polar groups –SO_3H had linked to its skeleton through the bonding function with carbon layer. And this will lead to the Brönsted acid site of a sulfate type carbon based solid acid catalyst will be easier to hydrate with water molecules, weakened or even lost its catalytic activity. Therefore, it is difficult to take into account the advantages of high catalytic activity and stability at the same time.

Recently, our research group prepared a solid acid catalyst from the employing of multi walled carbon nanotubes (MWCNTs) as support by impregnating it with concentrated sulfuric acid at high temperature. It was applied as catalyst for the synthesis of biodiesel from waste oils with high acid value and exhibited high catalytic activity [12]. However, due to so many hydrophilic polar groups -SO_3H had entered into the skeleton of MWCNTs through the bond combination action that was occurred between -SO_3H and carbon layer of MWCNTs, which has greatly enhanced the hydrophilic of this catalyst. Unfortunately, this obtained solid acid catalyst was consisted of Brönsted acid sites mainly. Hence, the hydration between Brönsted acid sites and water molecules will occur more easily. And finally, thereby weakening and even losing of its catalytic activity. Therefore, it is difficult to take into account the advantages of high catalytic activity and stability, simultaneously.

In this study, some methods were adopted to improve the catalytic stability of SO_4^{2-}/MWCNTs from the considering that Lewis acid site also has demonstrated high catalytic activity for esterification and transesterification [13–17]. Therefore, some metal cations with strong electron withdrawing effect can be tried to introduce at the same time while MWCNTs was modified with concentrated sulfuric acid at high temperature, which can be expected to affect the charge balance of –SO_3H and increase the trend of excess positive charge, so the type of acid sites will changed from Brönsted acid sites to Lewis acid sites. Therefore, this study attempts to introduce Al^{3+} for the influence of the charge balance of SO_4^{2-} when MWCNTs was modified with concentrated sulfuric acid at high temperature based on the considering of Al is an element with strong electron withdrawing effect. And eventually, it can be expected to increase the trend of excess positive charge, changing the type of acid sites of catalyst and obtaining of a novel solid Lewis acid catalyst Al^{3+}-SO_4^{2-}/MWCNTs.

2. Experimental

2.1. Reagent

$Al_2(SO_4)_3$ (99%, analytical pure) was purchased from Tianjin Hengxing Chemical Reagent Co., Ltd. China, concentrated sulfuric acid (99.9%, analytical pure) was purchased from Ganzhou Hongniu Instrument Co. Ltd. China, methanol (99%, analytical pure) was purchased from Tianjin Damao Chemical Reagent Factory of China, ethanol (99%, analytical pure) was purchased from Hengyang Kaixin chemical reagent Co. Ltd. China, diethyl ether (99.5%, analytical pure) was purchased from Xirong chemical engineering Co. Ltd. China, oleic acid (99%, analytical pure) was purchased from Xirong chemical engineering Co. Ltd. China, phenolphthalein (99%, analytical pure) was purchased from Tianjin Guangfu Fine Chemical Research Institute Co. Ltd. China.

2.2. Catalyst preparation

MWCNTs was produced by C_3H_6 decomposition on Fe/Mo/Al_2O_3 catalyst in a fluidized bed reactor (250 mm Inner Diameter, 1000 mm Height) with a sintered porous filter plate at its bottom. The plate was also acted as carrier for Fe/Mo/Al_2O_3 catalyst before it began to fluidize. At first, Fe/Mo/Al_2O_3 catalyst was placed into reactor; and then, C_3H_6 was employed as carbon source for the growth of MWCNTs, and which was pumped into the bottom inlet of the reactor under normal temperature and pressure with the flow rate of 5–10 $m^3\ h^{-1}$. While using the mixture composed of N_2 and H_2 for dilution, the flow rate is 1–3.5 $m^3\ h^{-1}$, the reaction temperature is maintained at the range of 500–700 °C and the reaction time is 30–60 min.

The preparation process of Al^{3+}-SO_4^{2-}/MWCNTs was carried out as follows: first, 1.0 g MWCNTs and 0.75 g $Al_2(SO_4)_3$ were added together in a 500 mL single neck round bottom boiling flask and mixed evenly, then adding 100 mL sulfuric acid; second, flask was placed in a ultrasonic cleaner by oscillating dispersion treatment for 30 min; third, flask was placed in a oil bath pot at 190 °C and stirred for 10 h, and the suspension was filtrated by pump after Al^{3+} and sulfuric acid-modified process had finished and the reaction liquid has cooled to room temperature. In order to ensure that the –SO_3H was not physically adsorbed on MWCNTs, the filter was repeatedly washed with de-ionized water. The 6 mol·L^{-1} aqueous $Ba(NO_3)_2$ solution was used to analyze the cleaning solution, and the washing can be stopped when precipitate did not appear. Finally, the cake was placed in the oven and dried for 12 h at 115 °C. Then, it was removed and ground to obtain Al^{3+}-SO_4^{2-}/MWCNTs catalyst.

Single walled carbon nanotubes (SWCNTs) and activated carbon (C) was also respectively impregnated with concentrated sulfuric acid and Al^{3+} for the preparation of Al^{3+}-SO_4^{2-}/SWCNTs and Al^{3+}-SO_4^{2-}/C catalysts. The process and conditions for the preparation of Al^{3+}-SO_4^{2-}/SWCNTs and Al^{3+}-SO_4^{2-}/C catalysts were the same as those of Al^{3+}-SO_4^{2-}/MWCNTs catalyst.

2.3. Catalyst characterization

Crystal structure of MWCNTs, SO_4^{2-}/MWCNTs and Al^{3+}-SO_4^{2-}/MWCNTs catalysts were analyzed by XRD (EMPYREAN, PANalytical). Cu Ka was used as the radiation source, tube pressure 40 kV, tube flow 40 mA, scanning speed 4° min^{-1}. Morphology of SO_4^{2-}/MWCNTs and Al^{3+}-SO_4^{2-}/MWCNTs catalysts were observed by TEM (Tecnai G2 F20, FEI). Raman analysis was performed on a laser confocal Raman spectrometer (LabRAM HR800, Horiba JobinYvon). The content of sulfur in various catalysts was analyzed by X-ray fluorescence spectrometer (Axios max, PANalytical). The acid strength of SO_4^{2-}/MWCNTs and Al^{3+}-SO_4^{2-}/MWCNTs catalysts were analyzed by NH_3-TPD using ammonia temperature programmed desorption analyzer (AutoChem II 2920, Micromeritics) in the temperature range of 0–800 °C. X-ray