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Amphiphilic Solid Basic Catalyst for Biodiesel Production: Synthesis and Characterization

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The research is focusing on the improvement of heterogeneous catalyst for biodiesel production application. An amphiphilic solid basic catalyst was prepared by using ZrO_2 as a support and modified by impregnation of KF and KOH. In order to study the effect of basic site, various loading of KF and KOH were used. The surfaces of KF/ZrO_2 and KOH/ZrO_2 particles were then tailored by alkylsilylation of n-octadecyltrichlorosilane (OTS) and chlorotrimethylsilane (CTMS). The resulting catalysts were characterized using nitrogen adsorption analysis, FTIR, TGA, XRD, SEM and TEM. Nitrogen adsorption isotherm revealed that the surface area were decrease respect to chemical modifications. FTIR and TGA confirm the attachment of alkylsilane on the surface of the particles and the alkylsilane loading were calculated as 5 wt%. XRD analysis reveals that there are no phase changes on the synthesized catalyst suggesting that ZrO_2 phase is stable towards modification. SEM micrograph shows an even particle distribution with an average diameter of 4.5 micron whereas TEM shows surface coverage was generated after alkylsilylation.

Keywords: Biodiesel, Heterogeneous Catalyst, Amphiphilic, Zirconia.

INTRODUCTION

Biodiesel is a renewable alternative to petroleum diesel and receive tremendous attention worldwide. The usage of biodiesel reduces emissions of hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter [1]. Besides, it is less toxic and biodegrades more rapidly compared to petroleum diesel [1]. Conventionally, alkyl ester is synthesized by a homogeneous-catalyzed transesterification reaction. Current method for production of biodiesel uses alkaline catalysts because the transesterification reaction is much faster as compared to acid-catalyzed reaction [2]. The homogeneous alkaline-catalyzed transesterification reaction usually uses sodium hydroxide as the catalyst [3]. Generally, basic catalysts yield higher conversion rates from triglycerides to methyl esters especially if the acidity index is higher than 0.5%. The alkaline catalysts show high yield of biodiesel with high quality, but causes a problem when the oils contain significant amounts of free fatty acids [4, 5].

Another problem in biodiesel transesterification is the water presence in acid-catalyzed reaction. Considering the strong affinity that sulfuric acid has for water, it is likely that the acid will interact more strongly with water

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compared to alcohol. Thus, if polar substance is present in the feedstock or produced during reaction, the acid catalyst will preferentially bind to water, leading to a reversible type of catalyst deactivation and generation of free fatty acids from triglycerides [6]. Based on the drawbacks from homogeneous-catalyzed acid and base reactions, we are proposing a new design of heterogeneous solid-base catalyst for biodiesel transesterification process since heterogeneous catalysts offer several intrinsic advantages over their homogeneous counterparts: including ease of product separation and catalyst recyclability. Thus, the main objective of this study is to synthesis phase boundary catalyst by using zirconia support for production of biodiesel via transesterification reaction. Amphiphilic zirconia impregnated with base (KOH, KF) presumably will catalyze the two immiscible reaction mixtures and enable the transesterification reaction to occur at low temperature with ambient pressure in a short reaction time.

METHODS AND MATERIALS

The chemicals used in this work are as follow: zirconium hydroxide (MEL Chemicals) as a catalyst support, potassium hydroxide (Merck) and potassium fluoride (Merck) was use as an alkaline source whereas cethyltrimethylsilane (Sigma-Aldrich) and octadecyltrichlorosilane (Sigma-Aldrich) as the alkylsilylating agents. In addition, toluene (Merck) and deionized water and toluene were used as a solvent in the catalysts preparation.

Catalyst Preparation

The KOH catalyst supported ZrO_2 was prepared by the impregnation method. Zirconium hydroxide powder was stirred in a certain volume of KOH solution with different concentrations at room temperature for 8 h and further dried at 100 °C overnight and finally calcined at 450 °C for 2 h. Similar procedure were repeated using different concentrations of KF. The prepared catalysts were subjected to surface modification using alkylsilanes (chlorotrimethylsilane, CTMS and octadecyltrichlorosilane, OTS). Modification is done by addition a small amount of water (~50w/w%) to the impregnated zirconia to aggregate the powder particles. In the second step, the wetted particles are immersed in 10 cm^3 toluene containing 500 μmol of CTMS or OTS, shake for several minutes and collected by centrifugation. The catalysts were then dried in oven for overnight.

Characterizations

The catalyst was characterized by nitrogen adsorption analysis using Micromeritics Tristar 3000. Fourier Transformed Infrared (FTIR) spectra were recorded using a Perkin Elmer Spectrum One spectrometer by KBr pallet method. Thermogravimetric Analysis (TGA) was carried out using Mettler Toledo TGA/SDTA 851 instrument, in range of 50 to 900 °C at a heating rate of 10 °C min^{-1} under air flow. X-ray diffraction (XRD) pattern was recorded on a Rigaku D/MAX-3B powder X-ray diffractometer with the Cu Kα radiation using an acceleration voltage of 40 kV and a current of 20 mA, in range $2\theta = 10°-70°$ at a scanning speed of 5°/min. The Scanning Electron Microscope (SEM) micrograph was investigated by a Carl *Zeiss* EVOm *SEM*, and Transmission Electron Microscope (TEM) was study using Carl Zeiss LIBRA TEM where a prepared sample were dispersed on ethanol and a drop of spent sample was deposited on the silica grid.

RESULTS AND DISCUSSIONS

Table 1 tabulates the surface properties that have been analyzed using nitrogen absorption analysis. Untreated ZrO_2 shows slightly higher surface area compared to the rest. After impregnation with base (KOH and KF), the surface area gradually decreased. Modification by OTS and CTMS were further reducing the surface area of the catalyst. One possible reason is the covering effect of the internal surface area of the catalyst by alkylsilyl groups. This is in agreement with what was reported by Mirji *et al.* where they found that the specific surface area of the modified SBA-15 was lower than the unmodified because the longer hydrocarbon tail in OTS that tend to accumulate at the exterior framework of the SBA-15 [7]. Therefore it is evident that deposition of alkali and attachment of functional groups (OTS and CTMS) occur on the surface of the ZrO_2.

TABLE 1
Specific surface area of the catalysts.

Sample	Surface Area (m^2/g)
ZrO_2	40.2
KOH/ZrO_2	22.6
KF/ZrO_2	32.3
$CTMS-KOH/ZrO_2$	10.2
$CTMS-KF/ZrO_2$	21.4
$OTS-KOH/ZrO_2$	13.4
$OTS-KF/ZrO_2$	12.6

FTIR spectra for $CTMS-KOH/ZrO_2$ and $OTS-KF/ZrO_2$ were recorded and are shown in *Fig. 1*. To further confirm the attachment of hydrophobic-inducing agent, we are focusing the study on the vibration of alkylsilane groups attached to the catalyst surfaces. Based to the spectra, its demonstrate the various C-H stretching vibrations at 2924 cm^{-1} for anti-symmetry stretching and 2851 cm^{-1} for symmetry stretching [8]. These C-H groups are from the alkyl chain of hydrophobic-inducing agent, i.e. the OTS and CTMS and conformed the successful attachment has been carried out in the modification process.

The XRD diffractograms of unmodified ZrO_2 support, modified KOH/ZrO_2, KF/ZrO_2 and $OTS-KF/ZrO_2$ were obtained (data not shown) and the result indicate that the major peaks tend to appear at 2θ range of 20° to 40°. The X-ray diffractograms demonstrate that all the modified catalysts possess a similar crystalline structure with characteristic peaks at 28.2° and 31.5°, corresponding to the monoclinic phase of ZrO_2. Respect to the chemically and physically stable ZrO_2, there were no change on its structure suggest that ZrO_2 support is highly stable to alkaline addition and alkylsilylation modifications. Despite the reduction on the peak intensity after the modifications, no new peaks of KOH and KF was recorded which suggested that the base particle were evenly distribute on the support.

Thermogravimetric analysis of ZrO_2, $CTMS-KF/ZrO_2$ and $OTS-KF/ZrO_2$ are shown in *Fig. 2*. The thermal analysis was carried out in the temperature range from 50 to 800 °C, in air at a heating rate of 10 °C/min. Unmodified ZrO_2 shown no significant weight loss on the analysis since it doesn't contain any additional substance. For the alkylsilylated catalysts, the main weight loss can be observed in range of 280 – 400 °C [7]. In this temperature, alkylsilane are decomposed where about 2.5% and 4.8%

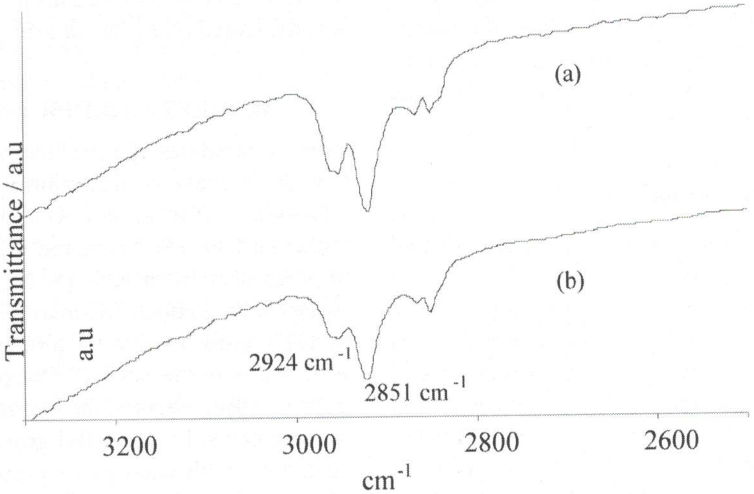

Fig. 1: FTIR spectra of (a) CTMS-KOH/ZrO2 and (b) OTS-KF/ZrO2

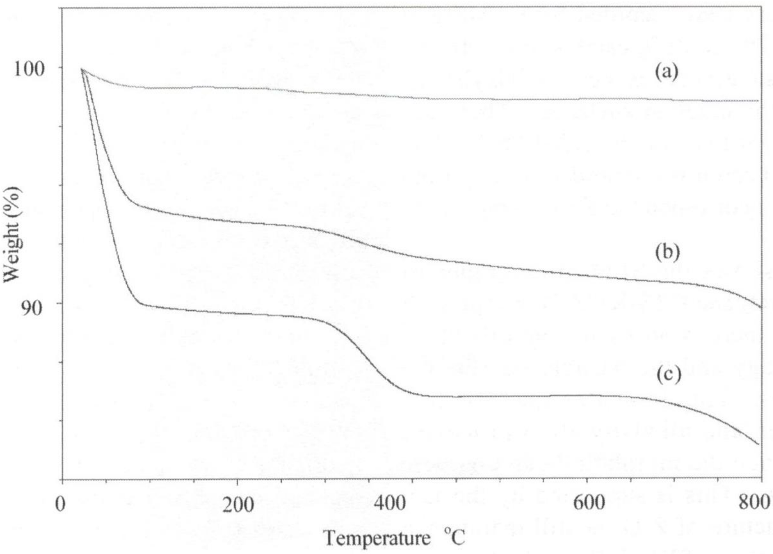

Fig. 2: Thermogravimetric analysis of (a) ZrO_2, (b) CTMS-KF/ZrO_2 and (c) OTS-KF/ZrO_2

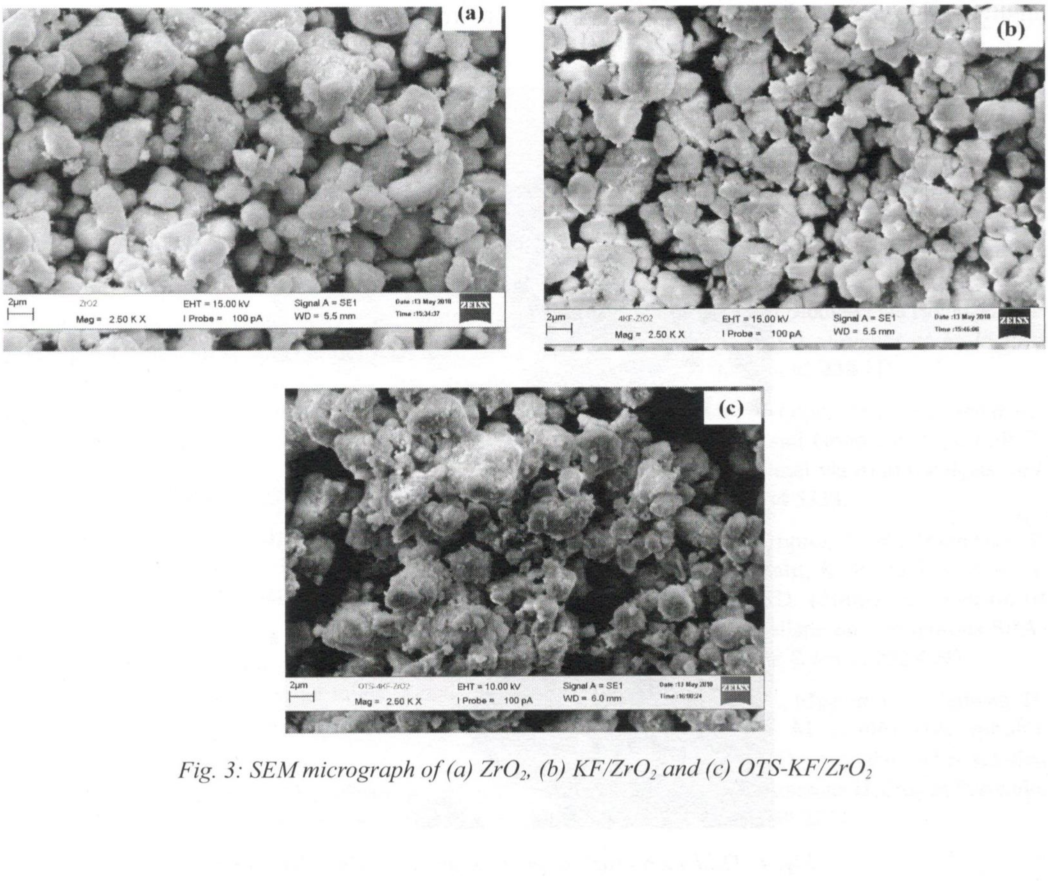

Fig. 3: SEM micrograph of (a) ZrO_2, (b) KF/ZrO_2 and (c) OTS-KF/ZrO_2

of weight loss were recorded for CTMS-KF/ZrO_2 and OTS-KF/ZrO_2 catalyst respectively. This would suggest the existence of alkylsilane groups on the catalyst surfaces. There are another weight loss was recorded for the KF/ZrO_2 catalyst and it was recorded starting from 650 °C which correspond to KF decomposition reaction.

Fig. 3 shows the SEM micrographs of ZrO_2, KF/ZrO_2 and OTS-KF/ZrO_2 samples. It reveals that there is no significant difference in morphology and the particle size among the samples. This indicates that alkaline modification and alkylsilylation processes did not change the morphology and particle size of ZrO_2. This is supported by the fact that the structure of ZrO_2 is still maintained after introduction of KOH, KF and alkylsilane groups. It is in agreement by XRD data where no phase changes were recorded. The samples also showed irregularity in their morphology in multi particle size distribution.

TEM micrograph of ZrO_2 and OTS-KOH/ZrO_2 was shown in *Fig. 4*. The surfaces of unmodified ZrO_2 show clean and clear its outer layer whereas for alkylsilylated ZrO_2 was shown a formation of new or bilayer outer surfaces. It was indicated that successful attachment of alkylsilane groups on support surfaces. Respect to the properties of the synthesized catalyst, it were targeted to produce synergetic effect for the biodiesel production. As the starting substrate of oil and methanol will resulted in the formation of bilayer mixture (*Fig. 5*), the synthesized catalysts will has the capability to be allocate at the interface since it has both hydrophilic and hydrophobic properties. Hydrophobic area is required to improve the adsorption of the organic substrates (oil) and alcohol (methanol) onto the surface of catalyst and secondly, it has the capability to protect the active sites from being deactivated. In the other hand, the hydrophilic area will enhance attractive force for methanol in order to increase the reaction performance.

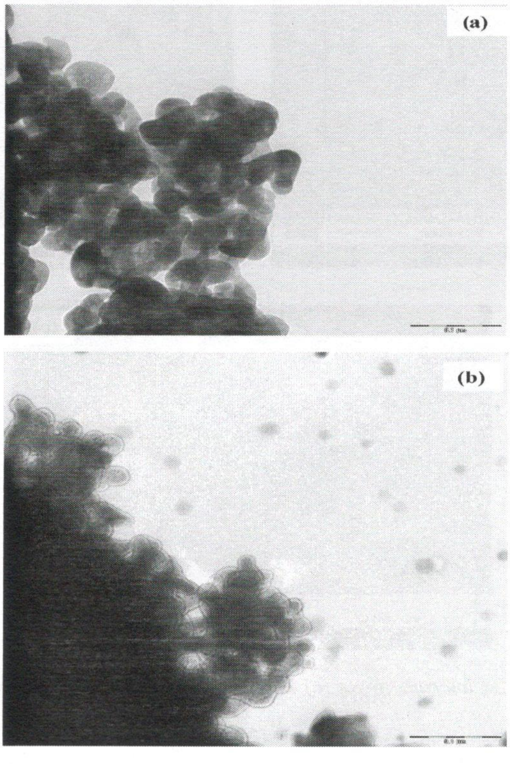

Fig. 4: TEM micrograph of (a) ZrO_2 and (b) OTS-KOH/ZrO_2

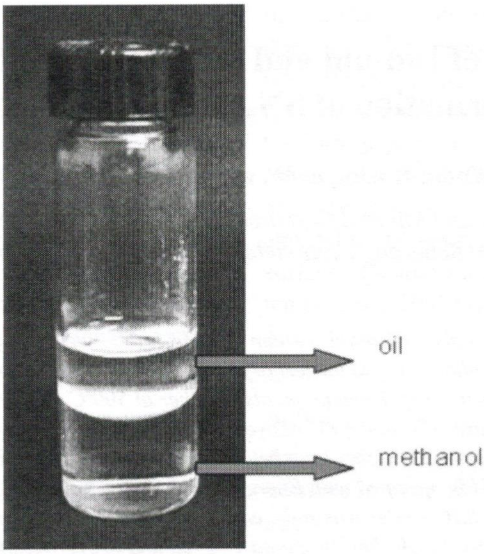

Fig. 5: Bilayer formation of oil-methanol mixture

CONCLUSIONS

Amphiphilic KOH/ZrO_2 and KF/ZrO_2 was successfully synthesized through alkaline impregnation and alkylsilylation. Based on the investigated properties, it would be able to be used as a promising catalyst for biodiesel production.

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