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The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel

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Abstract

Biodiesel produced by the transesterification of vegetable oils (VOs) has recently become more attractive on account of its environmental and economical benefits. In this work, a heterogeneous catalyst system was developed for the production of biodiesel from used VOs using a continuous process. The free fatty acids (FFA) contained in the used VOs, which cause several severe problems in transesterification catalysis, were converted to fatty acid methyl esters (FAME) before the main biodiesel production process. The activities of several heterogeneous catalysts on the conversion of FFA were tested, with a WO_3/ZrO_2 catalyst finally being selected. A method for preparing pellet-type catalysts was also developed. The pellet-type WO_3/ZrO_2 catalyst showed highly active and durable catalytic activities in the continuous flow process. The steady state conversion of ca. 70% was obtained in a 140 h durability test. The acidic property and catalytic activity of WO_3/ZrO_2 were attributed to the oxidation state of tungsten.

Keywords: Biodiesel; Esterification; Tungsten oxide zirconia; Heterogeneous catalyst

1. Introduction

Over recent decades, considerable effort has been made to develop clean and renewable fuels. Among the many possible sources, biodiesel fuel derived from vegetable oil (VO) has attracted attention as a promising substitute for conventional diesel fuels. The biodiesel produced by the transesterification of vegetable oils has recently become more attractive on account of its environmental benefits and the fact it is made from renewable resources. The continued increase in the consumption of petroleum has led to an increase in air pollution and accelerated global warming due to the increase in atmospheric CO_2. If biodiesel were to be used as an alternative fuel, the production of CO_2 would not increase because as the CO_2 emitted from biodiesel would be recovered through the production of biomass (feedstock of biodiesel). Furthermore, biodiesel contains no sulfuric compounds, which would lead to zero SOx production. Biodiesel contains more than 10% oxygen, which would increase the rate of complete fuel combustion and reduce the production of pollutants, such as THC, CO and PM. However, the temperature within the cylinders of a vehicle fueled with biodiesel would increase due to the enhanced combustion. This increased temperature stimulates the production of NOx, which results in a small increase in NOx emission compared to those produced from conventional diesel fuel.

Biodiesel is generally produced by the transesterification of triglycerides and methanol to form methyl esters, using a homogeneous catalyst, such as sodium or potassium hydroxide dissolved in methanol. An environmentally benign process for the production of biodiesel from VOs, using a heterogeneous catalyst, was recently developed in our previous study [1]. A $Na/NaOH/\gamma\text{-}Al_2O_3$ heterogeneous base catalyst was first used in the production of biodiesel. The use of used VO as feedstock has been suggested to reduce the production cost of biodiesel. However, used VOs contain free fatty acids (FFA) that can react with the base catalyst resulting in an inefficient target reaction and the production of soap as a by-product, which would

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eventually deactivate the base catalyst. Therefore, the FFA in used VOs should either be removed or converted to an inert or useful material in order to overcome these problems. In this study, attempts were made to convert the FFA to fatty acid methyl esters (FAME) using heterogeneous acid catalysts (Eq. (1)), which are themselves components of biodiesel [2]. Strong solid acid catalysts, such as Cs-heteropoly acid, H-zeolite, SO_4^{2-}/ZrO_2, SO_4^{2-}/Al_2O_3, SO_4^{2-}/SiO_2 and WO_3/ZrO_2, were tested for this esterification [3–6].

Of the catalysts tested, the WO_3/ZrO_2 catalyst was selected due to its high activity and stability. In this study, the reaction conditions were optimized, and the long-term activity of the catalyst was evaluated. SEM, ICP, XRD, BET and XPS analysis were used to characterize the WO_3/ZrO_2 catalyst.

$$\underset{\text{FFA}}{R_1{-}CO{-}OH} + \underset{\text{Alcohol}}{ROH} \overset{\text{Catalyst}}{\rightleftarrows} \underset{\text{Biodiesel}}{R_1{-}CO{-}O{-}R} + \underset{\text{Water}}{H_2O} \quad (1)$$

2. Experimental

2.1. Preparation of catalyst

The methods used for preparing the Cs-heteropoly acid, SO_4^{2-}/ZrO_2, SO_4^{2-}/Al_2O_3, SO_4^{2-}/SiO_2 and WO_3/ZrO_2 (powder type) are described in detail elsewhere [7]. The H-zeolite was purchased from ZEOLYST. The pellet-type WO_3/ZrO_2 was prepared by steaming the ZrO_2 pellets (Sud-Chemie) at 190 °C, with the ZrO_2 pellet impregnated with an appropriate concentration of an aqueous solution of ammonium metatungstate hydrate (Aldrich, 99.9%). The mixture was stirred for 2 h, and the excess water removed under vacuum at 80 °C. The final catalysts were obtained after calcination at 800 °C for 5 h under atmospheric conditions.

The BET surface area and average pore size of the powder WO_3/ZrO_2 catalyst were 57 m^2/g and 130 Å, respectively, while the pellet-type WO_3/ZrO_2 showed 40 m^2/g and 110 Å.

2.2. Esterification

The esterification was carried out at 75 °C in a 100 ml batch reactor, with constant stirring at 600 rpm for 1 h. 0.2 g of catalyst per ml of oil was used. A packed-bed continuous flow reactor was employed for a long-term operation of 140 h at 75 °C for 1 h using a feed of 4 wt% oleic acid to simulate the FFA in VOs. Fig. 1 shows the apparatus used in the reaction test. The methanol was loaded in excess (oleic acid:methanol = 1:19.4 mole ratio). The conversion of oleic acid to the methyl ester was calculated by titration with a 0.1 M KOH standard solution, according to Eq. (2) [7].

$$\text{Conversion}\,(\%) = \frac{\text{Initial acid value} - \text{final acid value}}{\text{Initial acid value}} \times 100\%$$
$$\text{Acid value} = \frac{M \times A \times F \times N}{S} \quad (2)$$

where M is the molecular weight of KOH; A the amount of KOH standard solution used in the titration; F the concentration coefficient of the KOH standard solution; N the normal concentration of the KOH standard solution; S is the sample weight.

2.3. Characteristics of the catalysts

The X-ray diffraction (XRD) patterns of the catalysts were obtained using a Rigaku D/max 2000 ultima plus diffractometer (monochromatic nickel filter, Cu Kα radiation).

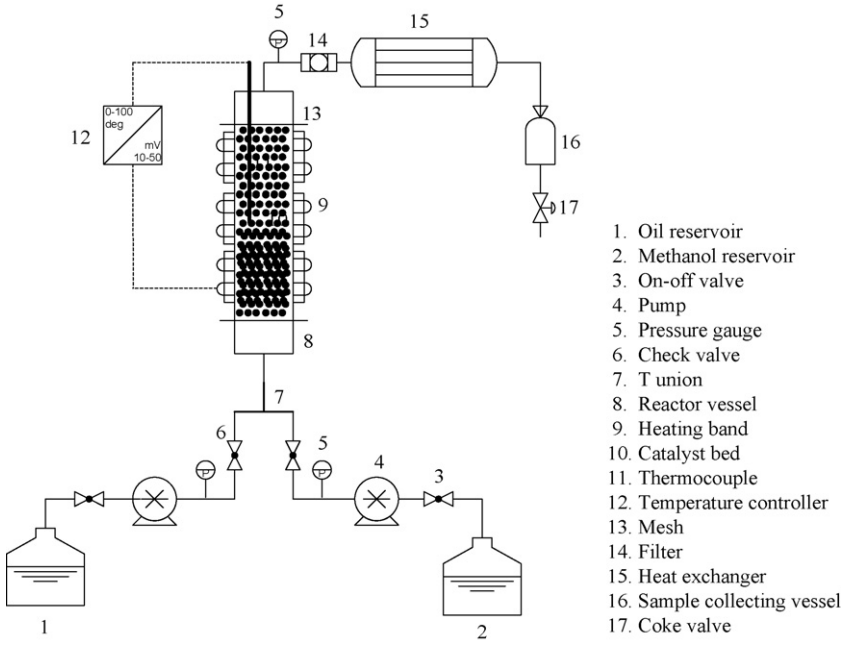

Fig. 1. The apparatus of the packed-bed reactor for the continuous production of biodiesel.

An FT-IR spectrometer (Perkin-Elmer Spectrum GX1) was used to acquire the transmission spectra.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, 138 Ultace, Jobin Yvon) analyses were carried out to determine the composition of the catalyst.

The morphology and composition of the catalysts coated onto carbon paper were examined by scanning electron microscopy (SEM, HITACHI S-4300).

The XPS spectra were recorded on a PHI 5800 ESCA system, equipped with a monochromatized Al Kα X-ray source of 1486.6 eV. The binding energies were referenced by setting the CH_χ peak maximum in the resolved C 1 s spectra to 284.6 eV. The WO_3/ZrO_2 was introduced into the preparation chamber of the spectrometer under UHV.

The acidity of the catalysts was measured using the temperature programmed desorption of NH_3 (NH_3-TPD) within a Stainless steel 3/8 in. reactor equipped with an on-line gas chromatograph (Agilent 6890N) and a mass spectrometer detector (Agilent 5975). The catalyst was pretreated at 120 °C for 2 h, under a flow of He, cooled to room temperature, and then heated to 700 °C at 1 °C/min, with a ChemStation used to collect the signals from the thermal conductivity detector (TCD).

3. Results and discussion

3.1. Reaction

In order to confirm the conversion of FFA, several heterogeneous catalysts were examined using an autoclave batch reactor. As shown in Fig. 2, SO_4^{2-}/ZrO_2 and WO_3/ZrO_2 showed the highest activity of the powder-type catalysts tested. WO_3/ZrO_2 was chosen as the catalyst for the longer operation test. With SO_4^{2-}/ZrO_2, there is the potential for the loss of SO_4^{2-} from the SO_4^{2-}/ZrO_2 into the liquid-phase reaction.

A packed-bed continuous flow reactor was designed for the continuous production of biodiesel from used oil, as described in Fig. 1. A powder-type catalyst was considered unsuitable for this reactor because it could potentially block the reactor during continuous operations. A method was developed for preparing the impregnation of WO_3 after steam treating the ZrO_2 pellets, as described in Section 2. In our previous work [7], WO_3/ZrO_2 was synthesized in powder form. The ZrO_2 support was prepared using $Zr(OH)_4$, with the formation of –OH bonds on its surface being essential for its catalytic activity. Therefore, in this study, additional steam treatment of the ZrO_2 pellets was used to generate surface –OH bonds. Fig. 3 shows the FT-IR spectra confirming the increase in the –OH band (3400 cm^{-1}) intensity. Fig. 4 shows the results of the longer reaction test. With a residence time of 1 h, the initial conversion of FFA was 65%, which was lower than that obtained in the batch reactor test. After 20 h, the conversion increased to 85% but decreased and remained stable at approximately 65% thereafter. The reproducibility of this unique trend was confirmed by 4 separate experiments, which are shown in Fig. 4. In order to calculate the equilibrium conversion, we have come up with Gibbs free energy and enthalpy value through modeling using ''ProPred (pure component property prediction tool)'' program which was copyrighted by CAPEC(Computer Aided Process-Product Engineering Center). According to the prediction program, equilibrium conversion at the temperature of 75 °C was 99.9%. Consequently, the conversion in packed-bed reaction did not reach the equilibrium value.

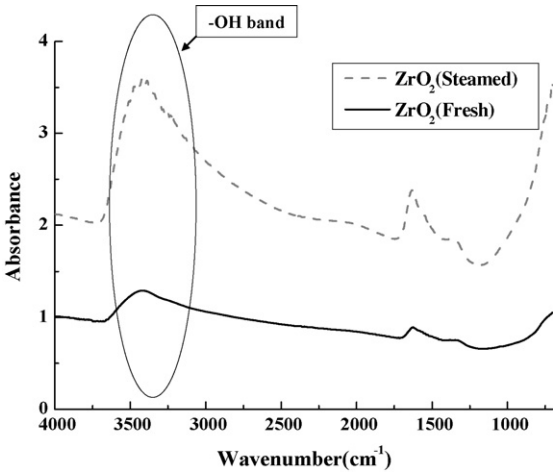

Fig. 3. The FT-IR analysis of the steamed ZrO_2.

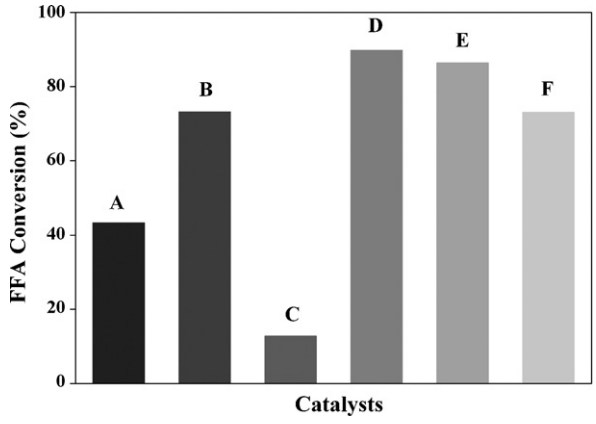

Fig. 2. FFA conversion over various powder-type catalysts; (A) SO_4^{2-}/Al_2O_3, (B) SO_4^{2-}/SiO_2, (C) H-zeolite, (D) SO_4^{2-}/ZrO_2, (E) WO_3/ZrO_2 and (F) Cs-heteropoly acid.

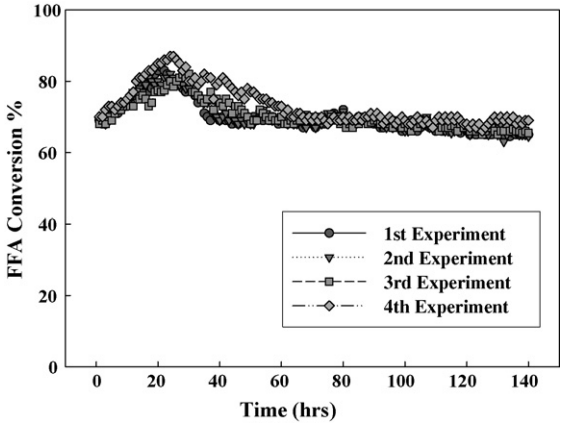

Fig. 4. Long-term reaction over the pellet-type WO_3/ZrO_2 catalyst.

The increase in FFA conversion during the 20 h reaction time was attributed to the following. The reactants consist of two substances, soybean oil and methanol. These two substances are less likely to mix with each other, which would decrease the level of FFA conversion a liquid–liquid reaction. An experiment was previously carried out on the miscibility of soybean oil and alcohol [1]. Hexane was found to be the most appropriate co-solvent. According to additional experiments, it was found out that biodiesel played a similar role as hexane. The biodiesel generated by a reaction between soybean oil and methanol improves the miscibility of the two substances and accelerates the reaction, which increases the level of FFA conversion.

Fig. 5 shows the catalyst activities at temperatures ranging from 75 to 200 °C. The initial conversion of FFA increased with increasing temperature but reached only 80% within 24 h. Subsequently, the level of conversion decreased and stabilized at approximately 65% after 140 h. But the final conversion of 200 °C rose by only 5% from that of 75 °C. This result of packed-bed reaction was very non-conventional. Catalytic activity, in common sense, should increase as temperature increases. However, the content of methanol (which is an important reactant) in the liquid phase decreased as the temperature was raised, because boiling point of methanol is 65 °C. We think this is the reason that increment of the activity was not so large.

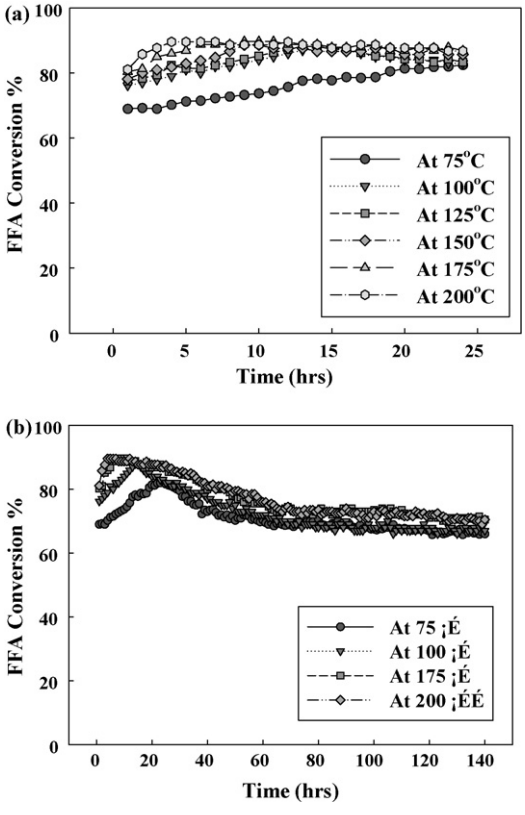

Fig. 5. Long-term reaction over the pellet-type WO_3/ZrO_2 catalyst at 75–200 °C; (a) reaction for 24 h and (b) reaction for 140 h.

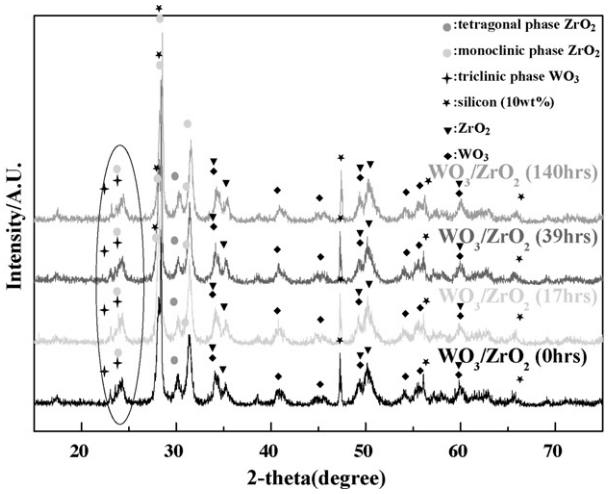

Fig. 6. XRD results for the pellet-type WO_3/ZrO_2 catalyst (at 75 °C reaction).

3.2. Catalyst characterization

The change in the catalyst structure with reaction time was examined by XRD. Fig. 6 shows the characteristic peaks of the tetragonal and monoclinic ZrO_2 and triclinic phase of WO_3 [8]. A slight change in the WO_3 peak was observed, even with increasing reaction time, which suggests that the decrease in catalyst activity was not related to the WO_3 structure.

ICP analysis was carried out to confirm the possibility of the leaching of catalysts, as shown in Fig. 7. As a result, it was verified that a minimal amount of W had leached. According to Fig. 7, the W/(W + Zr) ratio of catalyst was 10% before the reaction, 9.7% from the beginning to 20 h, and 9.5% at 140 h. The amount of W from 21 to 140 h remained relatively constant compared to that from initial time to 20 h even though the time period was five times longer. Overall, a small amount of W leaches during the initial 20 h with relatively no leaching thereafter. This means that W leaching is not the main reason for the decrease in catalytic activity.

Fig. 8 shows the SEM images of WO_3/ZrO_2. The particle size increases with time. XRD confirmed that there was no a particle growth or a phase transition (Fig. 6). The SEM image taken after re-calcining the catalyst after 140 h of reaction showed a similar morphology to that observed before the

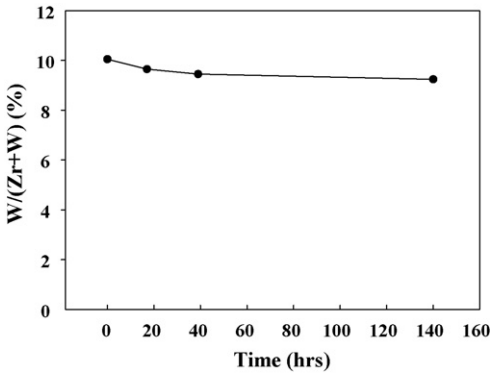

Fig. 7. ICP results for the pellet-type WO_3/ZrO_2 catalyst (at 75 °C reaction).

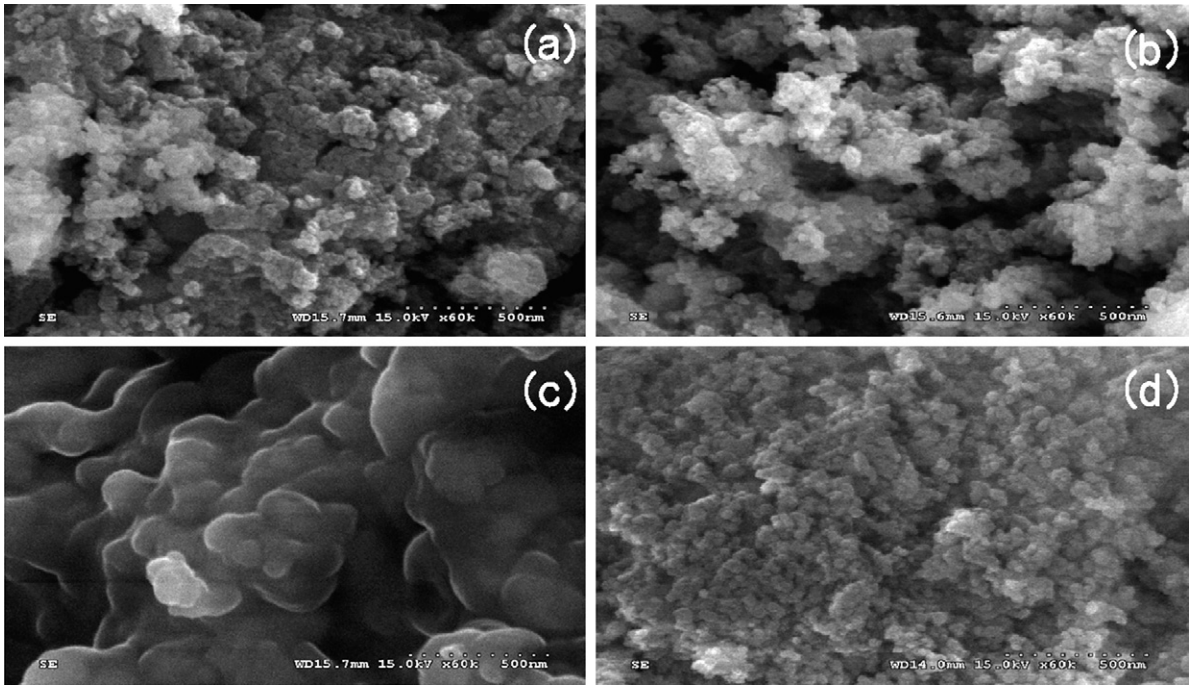

Fig. 8. SEM image of the pellet-type WO_3/ZrO_2 catalyst (at 75 °C reaction); (a) 0 h, (b) 17 h, (c) 140 h and (d) after re-calcination.

reaction. Hence, the SEM image does not show a morphological change but the regenerable deposition of soybean oil. Therefore, soybean oil (containing FFA) deposits onto the catalyst particles with increasing reaction time. However, as shown in Fig. 8d, the morphology of the re-calcinated catalyst was similar to that of the fresh catalyst (Fig. 8a).

The WO_3/ZrO_2 catalyst was combined by an interaction between the support and metal oxide. According to Ref. [5], the acid strength of the WO_3/ZrO_2 catalyst increases when WO_3 is impregnated. Therefore, it is believed that WO_3 is the major factor that determines the acidic properties of the catalyst. Accordingly, XPS analysis of the WO_3/ZrO_2 catalyst was performed. Fig. 9 shows the W (4f) XPS spectra of WO_3/ZrO_2. The binding energies of the W ($4f_{7/2}$) and W ($4f_{5/2}$) levels were

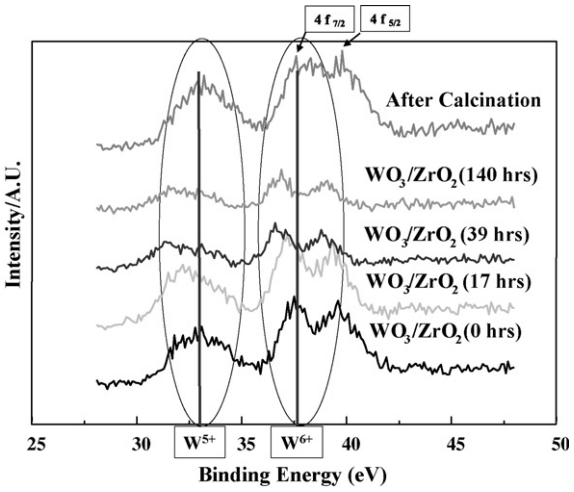

Fig. 9. XPS results of the pellet-type WO_3/ZrO_2 catalyst (at 75 °C reaction).

approximately 37.5 and 39.5 eV, respectively. As a result, from the beginning to 39 h of analysis there was partial WO_3 reduction. The binding energy W (4f) shifted to a lower energy. Oleic acid plays its role as a reducing agent in this reaction. Oleic acid is a free fatty acid which can weakly reduce WO_3. Even though the reduction is expected to be weak, the long time exposure of catalyst to oleic acid (much more than 17 h) can make catalyst reduced in a fair amount. Because the reduction potential of W^{6+} to W^{5+} is known to be a little smaller than that of W^{5+} to W^{4+} [9,10], reduction of W^{6+} is easier than that of W^{5+}. The reduction potential of W^{n+} decreases as reduction proceeds. For this XPS result, more aging (from 39 to 140 h) of catalyst could not shift the peak position any farther. We think that the reaction proceeds with partial reduction of catalyst. We also believe that a part of W^{6+} on catalyst surface was reduced to W^{5+}. If we accept this, the peak area of W^{5+} 4f should have increased slightly as the reduction proceeded, but the peak area of W^{5+} 4f decreased apparently as that of W^{6+} $4f_{7/2}$ did. The reason for this is the coverage of oil on the catalyst surface, which decreased the exposed amount of surface WO_3. This XPS result correlates with the result of the catalytic reaction of which FFA conversion decreased after 20 h. The binding energy of W (4f) did not change further from 39 to 140 h of the experiment. The catalytic activity was also the same. The binding energy of W (4f) in the re-calcinated catalyst after 140 h was identical to that of the fresh catalyst. The catalytic activity, of course, remained the same. Therefore, the reduction of WO_3 is one of the reasons for decrease in catalytic activity.

Fig. 10 shows that the initial 85% FFA conversion with the fresh catalyst decreased to 70% with proper aging. The aging performance was similar to that of the packed bed shown in Fig. 4. This decreased activity recovered to approximately 80%

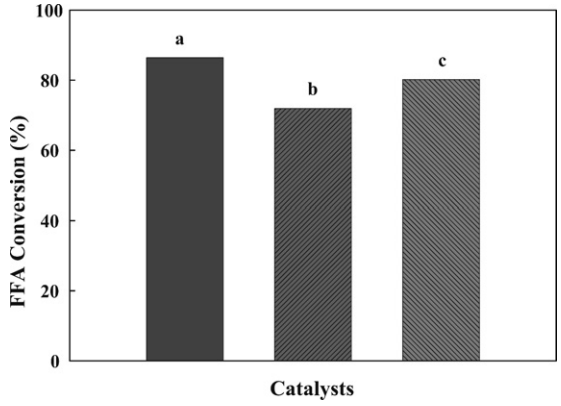

Fig. 10. FFA conversion over the WO_3/ZrO_2 catalyst (at 75 °C reaction): (a) fresh catalyst, (b) aged catalyst and (c) regenerated (air-re-calcinated) catalyst.

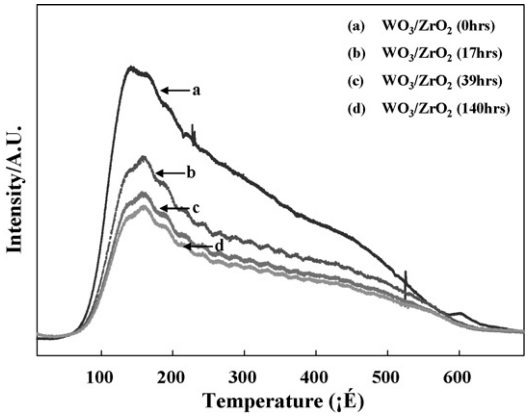

Fig. 11. TPD results of the pellet-type WO_3/ZrO_2 catalyst (at 75 °C reaction).

through re-calcination of the aged catalyst in air. Therefore, the decreased catalytic activity is mainly related to the reduction of WO_3, which can be restored through simple air calcination.

NH_3 TPD was performed to check the acid property of WO_3/ZrO_2 (Fig. 11). Hino and Arata reported that the WO_3/ZrO_2 catalyst contains strong acid sites [11]. The TPD profiles of the catalysts with different reaction times were obtained, with all samples showing broad TPD profiles, suggesting that the surface acid strength was widely distributed. The acid strength of the catalyst decreased with increasing reaction time but stabilized after 39 h. However, the relationship between the acidity and the oxidized state of WO_3 will require further study.

4. Conclusions

The SO_4^{2-}/ZrO_2 and WO_3/ZrO_2 catalysts were found to be effective in the esterification of FFA to FAME. However, SO_4^{2-}/ZrO_2 was not selected because of the potential loss of SO_4^{2-} in its liquid-phase application. The pellet-type WO_3/ZrO_2 catalyst was used for the longer reaction test. The result showed that 65% conversion could be maintained for up to 140 h. Powder-type catalysts were used for the batch reactions. However, pellet-type catalysts were used for packed-bed reactions because of the possible loss of catalyst and pressure drop with the powder-type catalyst. Thus, unlike powder-type catalysts, it was difficult to minimize the size of the catalysts that can be charged into the reactors. Because the pellet-type catalysts have a smaller BET surface area and lower pore size distribution than powder-type catalysts, they have a lower FFA conversion rate. In addition, there are mass transfer limitations because the size of catalysts used for packed-bed reactions is larger than that of the catalysts for batch reactions. This causes a decrease in FFA conversion. In conclusion, since the properties of the catalyst are different, it is difficult to compare batch reactions with packed-bed reactions. Packed-bed reactions have advantages over batch reactions in terms of mass production but have some disadvantages when their activity is considered. Therefore, optimization of the catalyst pellet size will be needed to maximize the activity of the catalysts. This will be examined in future studies.

From the characterization results, the oxidation state of W is mainly related to the catalytic activity of WO_3/ZrO_2. The activity could be regenerated through simple air re-calcination. The TPD results indicated that the surface acid strength was distributed widely. Moreover, there was a decrease in acidity with decreasing catalytic activity, which appears to be related to the oxidation state of the tungsten.

Acknowledgements

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