

Catalytic effect of $\text{CeO}_2\text{-Fe}_2\text{O}_3$ on transesterification in High-temperature high-pressure methanol

(高温高压メタノール中でのトランスエステル化における $\text{CeO}_2\text{-Fe}_2\text{O}_3$ の触媒効果)

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1. Introduction

Biodiesel, a mixture of alkyl esters, is an alternative biomass fuel derived from vegetable oils and animal fats. In the conventional biodiesel production process, triglycerides from fats and oils are converted to alkyl esters by a catalyzed transesterification. Although the reaction itself is easy to carry out, the subsequent steps of neutralization, separation and purification generate considerable amounts of highly corrosive wastewater [1]. The use of heterogeneous catalysts instead of homogeneous catalysts is gaining popularity since the approach facilitates catalyst separation and purification [2].

However, some metal oxide catalysts are not stable in methanol, some active oxide components are moisture sensitive and rapidly leached by methanol [3], limiting their applicability. Organic reactions using solid catalysts also have slow reaction rates in methanol at normal temperature due to the high diffusion resistance of methanol molecules [4]. High-temperature and high-pressure methanol has a lower viscosity and a higher diffusion rate than room temperature methanol, therefore catalyzing with heterogeneous catalysts in this state both increases the reaction rate and facilitates subsequent separation.

It was also discovered that using mixed metal oxides as catalysts resulted in higher yields than that of pure metal oxides [5]. Due to their intermolecular interactions, complexes of metal ions and loaded solid base catalysts can acquire certain structures that not only increase stability but also have better catalytic activity. The citrate process, which promotes the dispersion of the active component particles and the enrichment of the active component particles on the surface of the catalysts as compared to the conventional impregnation method, is able to prevent the aggregation of metal ions in the preparation of composite metal oxide catalysts because the molecular structure of citrate is significantly larger than that of nitrate. Therefore, it is very meaningful to investigate mixed metal oxide catalysts for transesterification under high temperature and high pressure methanol.

2. Research Purpose

The present study is to discuss the catalytic transesterification of mixed metal oxides at high-temperature and high-pressure methanol aiming to increase the rate, yield and stability of the reaction while decreasing the temperature and pressure. The transesterification reaction of ethyl laurate and methanol was used as a reaction model in this study. The candidate catalysts were ten composite metal oxides $\text{CeO}_2\text{-Fe}_2\text{O}_3$ with different CeO_2 and Fe_2O_3 ratios. The basicity and

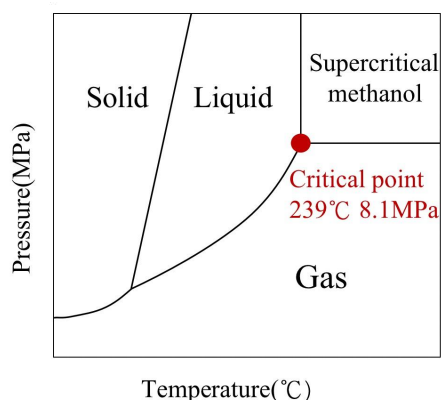


Fig. 1 The state of Methanol

stability are enhanced by compounding the two oxides. Yields, conversions and catalyst characterization were determined at different temperatures, pressures and times to investigate the ratio of Ce to Fe in the catalyst at optimum catalytic efficiency.

3. Experimental Methods

3.1 Catalyst preparation

The $\text{CeO}_2\text{-Fe}_2\text{O}_3$ was prepared by citrate process^[6]. To prepare $\text{CeO}_2\text{-Fe}_2\text{O}_3$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (the molar ratio Fe from 0%-100%) and the same mol of citric acid were mixed. After stirring and melting at room temperature, then heated at 70°C with water bath. Next it was heated at 170°C for 2 hours, and then it was transferred to a crucible and calcined at 550°C for 2 hours. At last, $\text{CeO}_2\text{-Fe}_2\text{O}_3$ was obtained after cooling down.

3.2 High-temperature and high-pressure methanol-catalyzed transesterification

This experiment was carried out using the electrical heated shaking batch reactor shown in Fig. 2. The reaction pressure was adjusted by the density of the reaction feedstock. The methanol and ethyl laurate were mixed in a molar ratio of 1:100 in supercritical methanol at 250°C 10 MPa and subcritical methanol at 200°C 6 MPa, respectively. The reactor was heated and stirred (100 times/min) after the temperature was stabilized. After heating for the specified time, the reactor was removed and cooled in water for at least 5 minutes. After removing the sample from the reactor, the reactor was cleaned with the organic solvent in ethanol and then the cleaning solution was added to the sample. The reacted product sample is filtered using a filter syringe. The reacted catalyst was recovered through a centrifuge and dryer. The dried pellets were analyzed for their crystal structure by XRD. The reaction rate was determined by measuring the concentration of ethyl laurate remaining in the filtered solution, and the concentration of methyl laurate produced determined the yield.

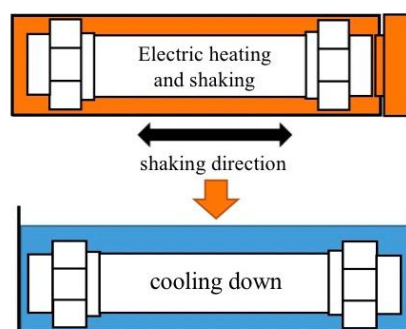


Fig.2 Procedure of experiment

After removing the sample from the reactor, the reactor was cleaned with the organic solvent in ethanol and then the cleaning solution was added to the sample. The reacted product sample is filtered using a filter syringe. The reacted catalyst was recovered through a centrifuge and dryer. The dried pellets were analyzed for their crystal structure by XRD. The reaction rate was determined by measuring the concentration of ethyl laurate remaining in the filtered solution, and the concentration of methyl laurate produced determined the yield.

4. Experimental results

4.1 Characterization of catalyst

a. Composition

Fig. 3 shows the XRD profiles of the $\text{CeO}_2\text{-Fe}_2\text{O}_3$ peaks can correspond to CeO_2 and Fe_2O_3 , determine if the ratio of Fe to Ce is as expected. It also shows the XRD profiles of the catalysts with Fe contents of 0 mol%, 20 mol%, 40 mol%, 50 mol%, and 80 mol%, where the red line is the peak of Fe_2O_3 and the green line is the peak of CeO_2 . From this result, it can be determined that the Fe_2O_3 and CeO_2 peak areas and the content of the composite catalyst are in agreement, and the expected content of the two oxides in the produced catalyst corresponds.

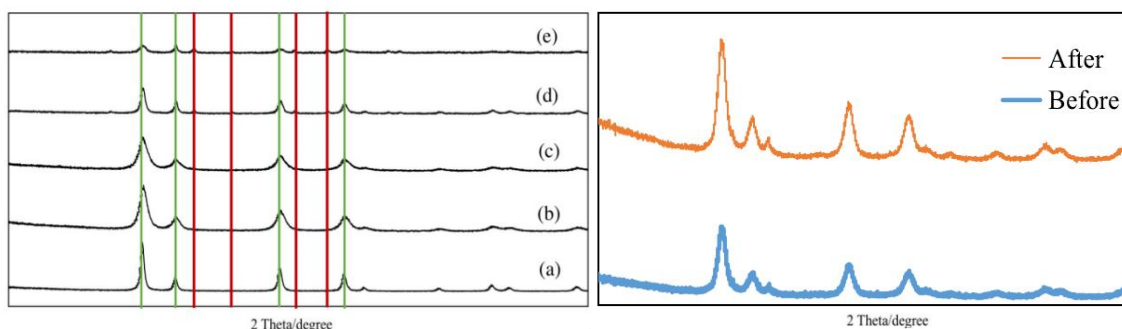


Fig. 3 XRD profiles of $\text{CeO}_2\text{-Fe}_2\text{O}_3$ samples, Fe content: (a) 0 mol%, (b) 20 mol%, (c) 40 mol%, (d) 50 mol%, (e) 80 mol% (Red line: peak of Fe_2O_3 Green line: peak of CeO_2)

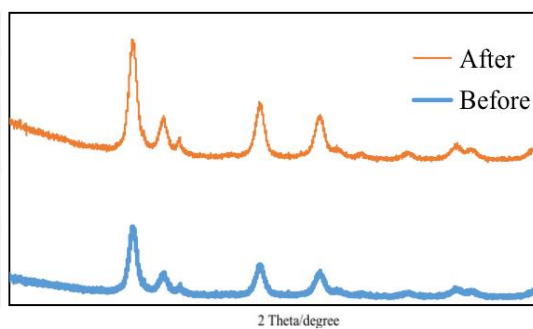


Fig. 4 The XRD profiles of 50 mol% Fe before and after the reaction

b. Stability

Since the experiments in this study were carried out in methanol at high pressure and high temperature. Therefore, it was necessary to determine whether the prepared $\text{CeO}_2\text{-Fe}_2\text{O}_3$ could be stable in supercritical methanol before starting the experiments. In this experiment, the maximum reaction temperature was 250°C and the maximum reaction time was 90 minutes. The catalyst stability experiment was stirred at 250°C for 120 minutes to see whether $\text{CeO}_2\text{-Fe}_2\text{O}_3$ could exist stably after reaction. The XRD profiles of $\text{CeO}_2\text{-Fe}_2\text{O}_3$ before and after the reaction are shown in Fig. 4. The peaks of the two plots are basically identical, which can confirm that the crystal structure of $\text{CeO}_2\text{-Fe}_2\text{O}_3$ is stable at high temperature and pressure.

c. CO_2 -TPD and BET surface area

Temperature Programmed Desorption (TPD) of CO_2 adsorbed on the $\text{CeO}_2\text{-Fe}_2\text{O}_3$ was measured to characterize the basicity (Fig. 5). It is conceivable that strongly basic sites peak at 600°C with 50 mol% Fe. Because the TPD peak plot for 60 mol% Fe and 50 mol% Fe are so comparable, the experimental results may be trusted more. A CO_2 desorption peak in pure CeO_2 at about 150°C (curve a) shows that it has weakly basic sites. 90 mol% Fe sample has two desorption peaks at around 100°C and 300°C (curve e) suggesting that the addition of Fe_2O_3 to CeO_2 alters the amount of CO_2 desorption up to 600°C . Fig. 6 shows the total number of basic sites and specific surface area of $\text{CeO}_2\text{-Fe}_2\text{O}_3$ samples. The number of basic sites reaches a maximum at 40-60 mol% Fe. The specific surface area also varies with Fe content. 50 mol% Fe mixed catalysts have a higher surface area than pure CeO_2 .

4.2 Reaction in supercritical methanol

In supercritical methanol, at 250°C , reactions with and without catalyst were investigated. Fig. 7 shows the time dependence of conversion and yield of ethyl laurate. Since the conversions and yields were very close, the transesterification reaction was considered to be the main reaction. It can be seen that at 90 minutes the conversion is high even without the catalyst. However, the use of a catalyst can shorten the reaction time while achieving the same conversion.

4.3 Reaction in subcritical methanol

Since good conversions have been achieved by no catalyzed transesterification in supercritical methanol, this experiment aims to lower the temperature (subcritical methanol) while using catalysts to achieve higher conversions. In subcritical methanol, the catalytic effect of 0 - 100

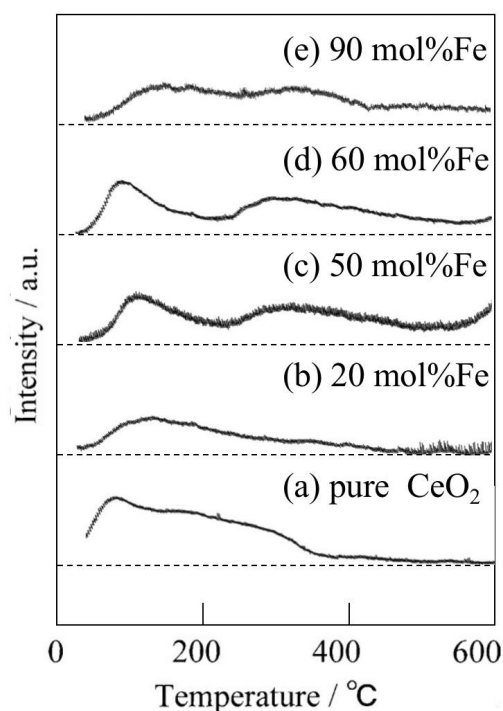


Fig. 5 TPD profiles of CO_2 adsorbed on $\text{CeO}_2\text{-Fe}_2\text{O}_3$ catalysts with different Fe contents: (a) Fe content: 0 mol%, (b) 20 mol%, (c) 50 mol%, (d) 60 mol%, (e) 90 mol%

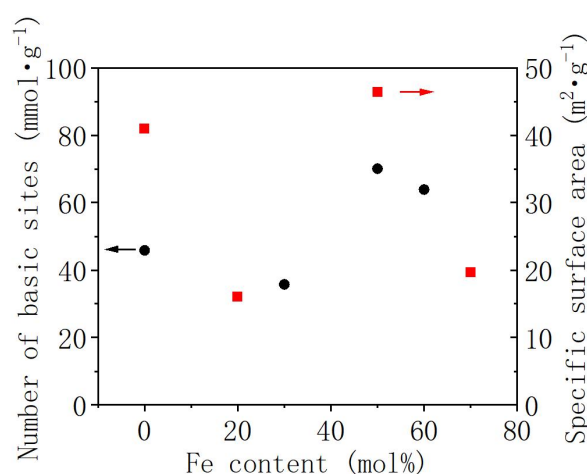


Fig. 6 Number of basic sites and specific surface area of $\text{CeO}_2\text{-Fe}_2\text{O}_3$

mol% Fe catalysts on ethyl laurate and the control group were measured at 200°C, 6 MPa. Their conversions and reaction rate constant are shown in Fig. 8. Up to 50% increase with Fe content, conversion rate gradually increases. Pure CeO₂ also has good activity. Above 50% increase with Fe content, conversion decreases. The activity of the catalyst reached its maximum at 50% Fe content, 90 min. It indicates that the addition of Fe increases the activity of pure CeO₂ catalyst. The composite catalyst is also more active than pure Fe₂O₃, indicating that the addition of CeO₂ improves the basicity of Fe₂O₃. Fig. 9 is first-order kinetic rate constant with different Fe content. From the results of CO₂-TPD, the basic sites are most abundant when the Fe content is 50%, followed by 60% and 0%, which also corresponds to the magnitude of the conversion and reaction rate constant of the catalytic transesterification under subcritical methanol. Moreover, the specific surface area was also greater than that of the composite catalyst with pure CeO₂ and other ratios when the Fe content of the catalyst was at 50% in the BET.

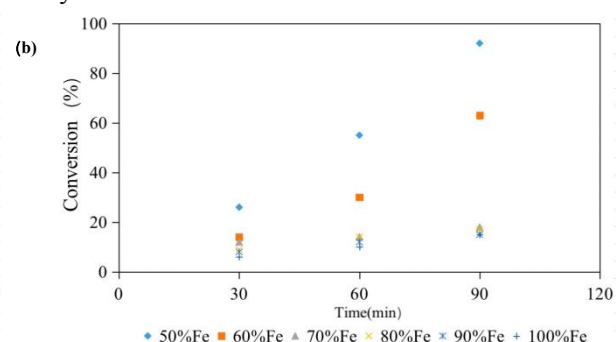
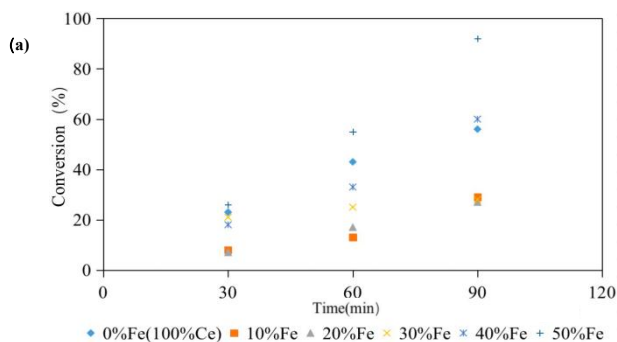


Fig. 8 Average conversion VS. Time with different Fe content (a) 0-50 mol% Fe (b) 50-100mol%Fe

5. Conclusion

In this study, a solid base-catalyzed reaction was carried out in methanol at high temperature and pressure using ester exchange reaction as a model reaction. The effects of changes in the metal ratio in the mixed metal oxide solid catalyst on the reaction rate were investigated using CeO₂ and Fe₂O₃, and the effects of different reaction temperatures, reaction pressures and time changes on the reaction rate were also investigated. The results pointed out that the composite catalysts have higher catalytic efficiency compared to single metal oxide catalysts. Transesterification is important in the production of biodiesel and so on, and this study is expected to provide a theoretical basis for faster reaction rates and to provide a theoretical basis for such reactions.

Reference

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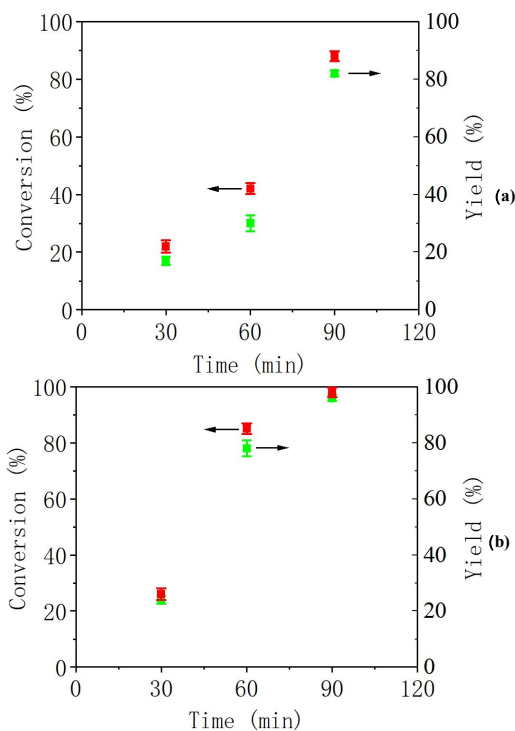


Fig. 7 Time dependence of yield, conversion and reaction rate constant (a) no catalyst (b) 50 mol% Fe (●) conversion (■) Yield

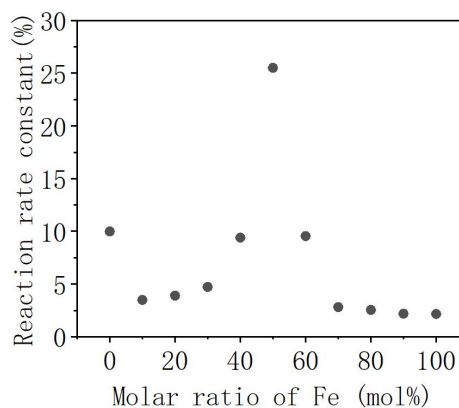


Fig. 9 Reaction rate constant for different Fe content catalysts