

Department of Environment Systems

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Master's Thesis

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

**(高温高圧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

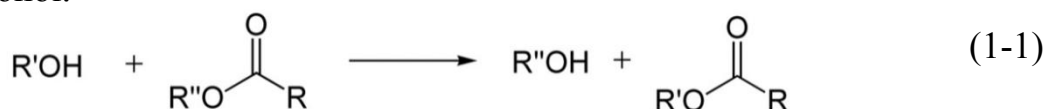
1.1 Biodiesel

With the onset of an energy crisis, people's attention has switched away from restricted petroleum supplies and toward animal and vegetable oils.^[1] Unprocessed animal and vegetable oils, on the other hand, can only be utilized in diesel engines for a limited time. This is due to the fact that animal and vegetable oils include compounds with varying degrees of saturation, which can produce lubricating oil aggregation in diesel engines. Furthermore, the molecular structure of animal and vegetable oils differs from that of diesel, which can cause problems like poor atomization, incomplete combustion, and nozzle blockage.^[2-4]

However, esterification of animal and vegetable fats with methanol or ethanol to produce fatty acid methyl or ethyl esters is regarded as an environmentally favorable biofuel. This biofuel, also known as biodiesel, can be utilized in the same way as diesel is. Biodiesel is a typical "green energy" product with environmentally friendly, engine starting, and fuel performance. It is strategically important in promoting economic sustainability, facilitating energy substitution, decreasing environmental strain, and regulating urban air pollution.^[5]

1.2 Transterification

Transterification^[6] of animal and vegetable lipids, which are glyceride molecules, is generally used in the production of biodiesel. Transterification process replaces glycerol in glyceride compounds with acid esters, resulting in ester compounds with lower viscosity and greater usefulness as fuel. Transterification works on the premise of adding a catalyst to enhance the reaction between glyceride molecules and alcohol. The alcohol exchanges with the acid esters in the glyceride compounds during the process, resulting in the creation of new ester compounds and glycerol. Methanol and ethanol are the most regularly utilized alcohols. (1-1) is the process of exchanging the organic functional group R'' of an ester with the organic group R' of an alcohol.



Biological enzyme and chemical catalysis are two traditional approaches for ester exchange reactions^[7].

1.2.1 Biological enzyme catalysis

Enzymes are natural biocatalysts^[8] with high catalytic activity and selectivity. Excellent substrate specificity, gentle reaction conditions, excellent product purity, and the absence of extra neutralizing steps^[9] are all advantages of utilizing biocatalysts in ester exchange processes^[10]. However, at industrial production scales, the stability and tolerance of biocatalysts in ester exchange reactions may be low, making them prone to inhibition or deactivation^[11]. This can lead to a shorter catalyst lifespan, requiring more frequent catalyst replacement or maintenance, which can have an impact on the overall economic feasibility of the manufacturing process. Furthermore, as compared to certain chemical catalysts, enzymes may have slower reaction rates, requiring longer production cycles^[12].

1.2.2 Chemical catalysis

The chemical catalytic^[13] ester exchange technology is mostly used in the present industrialized biodiesel synthesis process. Under the catalysis of alkali or acid catalysts, animal and vegetable oils/fats are reacted with low-carbon alcohols (such as methanol or ethanol) to undergo ester exchange reactions^[14]. This method yields fatty acid methyl or ethyl esters, which are then mixed to form biodiesel.

a. Homogeneous Catalysts

Homogeneous catalysts are those that are dissolved in the reaction solvent and are in the same phase as the reactants and products in the reaction system^[15]. Common homogeneous catalysts include alkaline catalysts such as sodium hydroxide (NaOH)^{[16][17]} and potassium hydroxide (KOH)^[18], as well as acidic catalysts such as sulfuric acid (H₂SO₄)^{[19][20]} and ammonium bisulfate (NH₄HSO₄)^[21]. High catalytic activity, exceptional selectivity, low cost, and ease of operation are some of the benefits of homogeneous catalysts. However, the catalysts are difficult to extract from the products and require additional processing, and certain catalysts are highly corrosive.^[22]

b. Heterogeneous Catalysts

Heterogeneous catalysts^[23] are those that exist in a distinct phase than the

reactants and products, typically in solid form. Solid acid catalysts^[24] such as solid acid ion exchange resins and cerium oxide, as well as solid base catalysts^[25] such as calcium oxide (CaO)^[26], magnesium oxide (MgO)^[27], and sodium oxide (Na₂O)^[28], are examples of heterogeneous catalysts. Their advantages include high catalytic activity, good selectivity, and ease of separation and recyclability. Furthermore, solid acid catalysts^[29] exhibit good stability and tolerance, allowing reactions to be conducted at higher temperatures. Solid base catalysts^[30], on the other hand, often have slower reaction rates and require longer reaction periods than homogeneous base catalysts. Solid base catalysts^[31] may deactivate during extended reactions, resulting in diminished catalytic activity. Additionally, greater reaction temperatures may be required for solid base catalysts to obtain optimal catalytic activity. The use of solid base catalysts^[32] may have environmental consequences, such as the disposal of used catalysts.

Table 1 Homogeneous catalysts in transterification^[15]

Alkaline catalysts	NaOH/ KOH	High catalytic activity, low cost, and easy accessibility.	The resultant products are difficult to separate from the catalyst and necessitate more catalyst removal.
Acidic catalysts	H ₂ SO ₄ / NH ₄ HSO ₄	High catalytic activity and selectivity.	Additional neutralization procedures are required to eliminate the produced acidic chemicals, and excellent corrosion resistance of the equipment and catalyst is required.

Table 2 Heterogeneous catalysts in transterification^[23]

Solid base catalysts		Good selectivity, and ease of separation and recyclability	Slower reaction rates and longer reaction periods than homogeneous base catalysts
Solid acid catalysts	CaO/ MgO/Na ₂ O	Good stability and tolerance at higher temperatures	Catalyst design and production are difficult, and reaction circumstances can affect the activity and durability of catalysts.

In summary, the chemical synthesis of biodiesel has the following disadvantages^[33]:

- (1) stringent controls on the water and free fatty acid content of the feedstock, which must be kept to less than 1%, necessitating preprocessing of the feedstock.
- (2) The use of alkali or acid as catalysts, which complicates the manufacturing process by necessitating additional steps for catalyst residue treatment and product purification. The disposal of waste alkali and acid solutions might result in secondary contamination.
- (3) Long process with various equipment involved, as well as the usage of catalysts, may raise production expenses, including catalyst procurement and waste disposal costs.

1.3 Supercritical methanol

The supercritical methanol method^[34] is an emerging technology for converting biomass into biodiesel. The supercritical methanol method^[35] is a supercritical transesterification reaction between the oil and grease components of biomass and methanol to form fatty acid methyl esters. Supercritical circumstances are defined as temperatures and pressures that exceed the critical point of the solvent, causing it to be both liquid and gaseous at the same time. Methanol's increased solubility and fluidity under supercritical conditions aid in improving the equilibrium conversion rate of the ester exchange reaction. This means that more reactants can be converted to products, increasing the efficiency of the reaction and the product yield. Second, methanol is a reaction medium as well as a reactant, which considerably enhances the reaction rate due to the significant rise in supercritical methanol solubility for oils and fats^[36]. The supercritical methanol-catalyzed ester exchange reaction can combine reaction and extraction in a single step, simplifying the manufacturing process. Supercritical methanol serves as both a solvent and a catalyst, allowing it to complete the esterification and product separation in a single step, avoiding the need for additional processing stages. The method can be employed without a catalyst, has low requirements for oil and grease raw materials, and has the advantages of not requiring pretreatment, having a short reaction time, being a simple

process, and emitting no pollutants^[37]. Additionally, there are several restrictions and difficulties associated with the supercritical methanol-catalyzed transesterification reaction. The catalyst-free supercritical methanol process has fairly high pressure, temperature, and alcohol-to-oil ratios, which necessitates massive methanol cycles and expensive equipment. The transesterification reaction with catalyst under supercritical methanol necessitates a high level of catalyst stability and lifetime. Methanol's high temperature and corrosiveness may damage or deactivate the catalyst, impacting regeneration and reuse^[38].

1.3.1 Properties of supercritical methanol

Comparison of some properties of supercritical methanol with methanol under normal conditions as shown in Table 3.

Table 3 Physicochemical properties of methanol in ordinary and supercritical conditions ^[39]

Properties	Ordinary condition	Supercritical condition (239 °C 8.1 MPa)
Specific gravity (kg · L ⁻¹)	0.7915	0.2720
Ionic product lgKw	-0.77	
Dielectric constant	32.6	7.2
Viscosity (Pa·s)	5.4×10^{-4}	5.8×10^{-5}
Hydrogen bonding number	1.93	< 0.7
Solubility parameter [(MPa) ^{1/2}]	7.1	4.1

a. Critical characteristics^[40]

When a gas is pressured, it normally transforms into a liquid, and at high temperatures, more pressures are required to change the gas into a liquid. Because the density of the liquid decreases as temperature rises, the densities of the gas and liquid steadily approach and eventually become identical. Critical temperature and critical pressure are the temperatures and pressures at which this occurs. A supercritical fluid is a non-condensable, dense fluid with a temperature and pressure that exceeds the critical temperature and pressure.

Figure. 1 shows the state of methanol. Under normal conditions, methanol is a volatile liquid (boiling point 64.7°C). The critical pressure of methanol is 8.1 MPa and the critical temperature is 239.4°C. Above this

temperature, the methanol liquid transforms into supercritical methanol rather than a gas. Furthermore, subcritical methanol is methanol that is below the critical temperature and pressure but at high temperature and pressure. High-temperature and high-pressure methanol are the collective terms for subcritical and supercritical methanol.

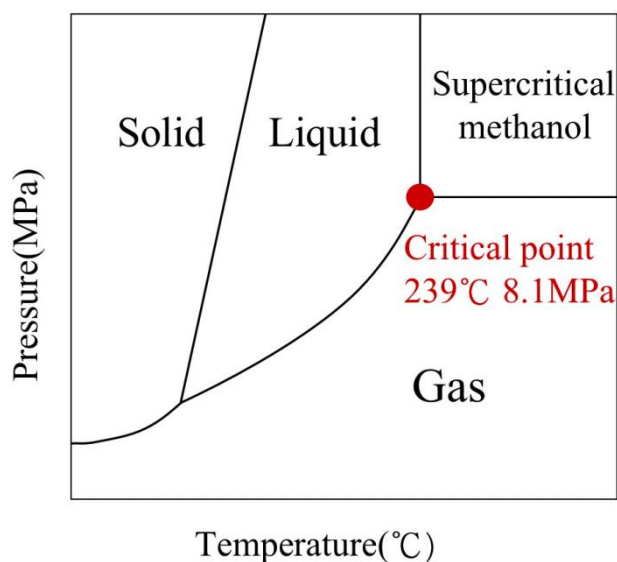


Fig. 1. The state of methanol

b. Ion product and hydrogen bonding

The ion product is a critical parameter in chemical processes. It fluctuates with pressure and temperature, with pressure having a greater effect on ion product; the higher the pressure, the larger the ion product. According to the literature^[41], the ion product of supercritical fluids increases dramatically with pressure. As a result, supercritical methanol has the same acid and base catalytic characteristics as supercritical water. At room temperature, methanol, like water molecules, easily forms hydrogen bonds between molecules, which require 5-7 kcal · mol⁻¹ of energy to break, and it is much weaker than chemical bonds (25 - 100 kcal · mol⁻¹). Hydrogen bonds weaken with increasing temperature, and about 70% of the hydrogen bonds of methanol break near its critical point; when the temperature rises to 300°C and the pressure is 10 MPa, only about 10% of intermolecular hydrogen bonds exist^[42]. Because of the large reduction of intermolecular hydrogen bonds in the supercritical methanol state, more methanol exists as individual molecules, which allows more methanol molecules to contact the reactants more easily and promote the reaction.

c. Viscosity and dielectric constant

Viscosity is the amount of resistance to the flow of a liquid, or the degree of viscosity of the liquid flow. Methanol's viscosity falls as temperature rises. This is because an increase in temperature enhances the thermal movement of molecules, resulting in fewer bonds between molecules and enhanced mobility, which leads to a drop in viscosity.

The dielectric constant^[43] is a quantity that evaluates a substance's dielectric characteristics and reflects the substance's capacity to respond to an electric field. The value of the dielectric constant represents the intensity of the electric dipole interactions between molecules or crystals in a substance. Methanol has a high dielectric constant because it contains polar chemical bonds. As the temperature rises, the thermal motion of the methanol molecules increases and the molecular connections weaken, resulting in a reduction in the dielectric constant.

The temperature dependence of the viscosity and dielectric constant of methanol has a reduced viscosity and dielectric constant in the supercritical state. The diffusion rate of reactants is faster with supercritical methanol as the reaction solvent at low viscosity than with methanol at room temperature. Because of the lower dielectric constant, the charge distribution and polarization in supercritical methanol are reduced, which aids in the reduction of charge interactions and binding. Reactant molecules and ions are freer to move and disperse. Furthermore, the decreased polar environment aids in the solubility of some non-polar compounds, making them easier to dissolve and react in supercritical methanol. Supercritical methanol's reduced charge polarization and interactions boost mass transfer. This is advantageous for reactions involving mass transfer processes between reactants and catalysts, as it can improve reaction uniformity and efficiency.

d. Supercritical methanol as both reaction medium and reactant

Supercritical methanol is not only a reaction medium, but it is also a reactant in most circumstances. Supercritical methanol can take part in a number of processes, including esterification, alcoholysis, and alkylation. Because supercritical methanol is both a reactant and a solvent in most processes, it frequently has a very high

concentration in the reaction system, which contributes significantly to boosting the reaction rate and increasing the conversion of the reaction.

1.4 Solid catalyst

A solid substance that speeds up a chemical process is known as a solid catalyst. Heterogeneous catalysts for supercritical methanol were used as solid catalysts in this work. They are extremely stable, selective, and active^[44]. Solid catalysts can be reused and are simpler to remove from the reaction product than homogenous catalysts. They can be used throughout a larger range of reaction temperatures and are more stable and active whether the reactants are gaseous or liquid. They are also extensively employed in a variety of industrial and academic domains. The following is a brief description of solid catalysts.

1.4.1 Catalytic mechanism

Solid catalysts speed up chemical processes by offering surface active sites that interact with the reactants physically or chemically, but they don't really change during or after the reaction. The typical catalytic processes and associated steps are as follows:

- a. Reactant molecules adhere to the catalyst surface by a process known as adsorption, which results in an accumulation of the molecules on the catalyst surface. Depending on the forces at work during the reaction between the reactants and the catalyst, adsorption can either be physisorption or chemisorption.
- b. Dissociation: The adsorbed reactant molecules split apart on the catalyst surface, generating reactive ions or groups that remain adsorbed. Reactive intermediates of reactants are produced by dissociation, which can reduce the reactant molecules into smaller pieces or ions and provide reactants for the following reaction stages.
- c. Intermediate formation: The reactant ions or reactive groups generated by dissociation interact with additional reactant molecules or species on the catalyst surface to form the reaction's intermediates. The intermediates are transient species of the process that have high reactivity and continue the reaction.
- d. Bond rearrangement: Intermediates undergo bond rearrangement on

the catalyst surface to form new chemical bonds and generate products. The bond rearrangement can include steps such as migration of atoms, bond formation and breaking, and the conversion of reactants to products is achieved by changing the connection of chemical bonds.

1.4.2 Acidity and basicity of solid catalyst

The active surfaces of a solid catalyst's acid-base sites often play an acidic or basic function in the catalytic reaction. The capacity of an acid site to deliver protons to a base site or to take electron pairs from a base site is a measure of its strength. The strength of a basic site is similar to how an acid site's ability to take protons from a base site or to supply electron pairs to a base site determines how strong an acid site is. The quantity of acid or base sites on the surface of a solid is known as its acid or base content. This quantity is typically stated as the quantity of acid or base sites per unit weight or unit surface area^[45].

The active sites on the surface of the solid are referred to as the type of acid or basic site. It consists of Lewis acid-base sites, Bronsted acid-base sites, as well as pairs of these bases (Bronsted acid-base pairs and Lewis acid-base pairs). In order to create an acid-base reaction, a Bronsted acid must accept an electron pair from the corresponding Lewis base. An acid-base reaction results from a Bronsted base giving a pair of electrons to the equivalent Lewis acid. A Bronsted acid-base pair is made up of a Bronsted acid and the related Bronsted base. Such acid-base couples are capable of completing acid-base reactions by transferring or sharing protons. Lewis acids and bases that match them can team up to generate Lewis acids and bases. By transferring electrons or exchanging electron pairs, such acid-base couples can finish acid-base processes. The acceptance and accessibility of protons or electron pairs is the key difference between a Lewis acid-base site and a Bronsted acid-base site. Lewis acid-base sites prioritize accepting and supplying electron pairs, whereas Bronsted acid-base sites prioritize accepting and supplying protons.

1.4.3 Designing and improving catalysts

Solid catalyst design and development^[46] is a significant area of study. By altering the composition, structure, and surface modification of catalysts,

the activity, selectivity, and stability of the catalysts can be increased. The reaction conditions, catalyst stability, and regenerative qualities should also be considered while choosing a catalyst. Current research also focuses on the synthesis of novel catalyst materials and the enhancement of catalytic lifespan^[47].

1.4.4 Evaluation of catalysts

Catalyst activity, selectivity, catalytic lifespan, and environmental dangers are all significant factors to consider when evaluating catalyst performance and applications.

The activity of a catalyst refers to its ability to promote a chemical reaction under specific conditions. A highly active catalyst reduces a reaction's activation energy, making the reaction easier to perform and raising the reaction rate. The activity of the catalyst is determined by its composition, structure, and surface qualities, as well as its interaction with the reactants.

A catalyst's selectivity refers to its capacity to produce a specified product during a catalytic reaction. A good catalyst can promote the production of desired goods while avoiding or reducing the generation of by-products. The stability and persistence of the catalyst during the reaction are referred to as its catalytic lifespan. A good catalyst should have a lengthy catalytic lifetime and be capable of retaining activity and selectivity over time. Catalytic lifespan is influenced by elements such as catalyst stability, toxin resistance, and corrosion resistance.

One of the variables to be examined is the environmental impact of the catalyst application. The toxicity of the catalyst itself, as well as the production of environmental contaminants, are both environmental dangers. A good catalyst should be ecologically safe, free of poisonous compounds, and capable of degrading or converting dangerous molecules properly.

There is a requirement in catalyst design and application to balance activity, selectivity, and catalytic lifespan while limiting environmental impact. Through the research and development of efficient, selective, and environmentally friendly catalysts, more sustainable, efficient, and green chemical reactions and processes can be realized.

1.5 Research Objective

1.5.1 Purpose

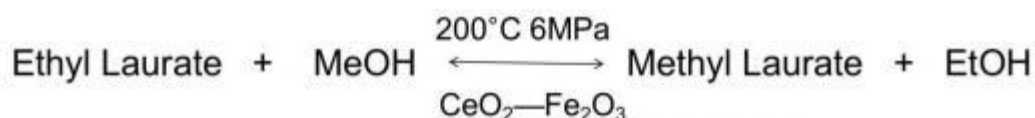
The purpose of this research was to determine the effects of temperature, different composite metal oxide solid catalyst ratios, and residence time on catalytic ester exchange processes in high temperature and high pressure methanol.

1.5.2 Candidate Catalyst

The composite cerium oxide iron oxide was utilized as a prospective catalyst in this study, and it was demonstrated that cerium oxide is basic and iron oxide is strongly reducing, and the composite catalyst remained very stable at 450°C, except for the pure Fe₂O₃. And the number of basic sites and specific surface area increased compared to pure CeO₂ and pure Fe₂O₃.

1.5.3 Reaction Model

Transterification is the exchange of triglycerides with methanol. Single-chain fatty lauric acid ethyl ester was selected as the reactant because the primary emphasis of this study was the catalytic effectiveness of the catalyst. Following is a description of the causes. Both ethyl laurate and supercritical methanol have boiling points of 269°C and 239°C, respectively. Accordingly, ethyl laurate can be used because the reaction begins when supercritical methanol is attained. While the three fatty acids that make up a triglyceride might individually be different, ethyl laurate only contains one fatty acid chain (-CH₂CH₂CH₃) in its composition. Because of this, there will be less adverse effects and byproducts, which will be helpful for a future investigation of the goods' conversion. In the illustration, the equation for ethyl laurate's ester exchange reaction is displayed. In this experiment, methanol serves as both the reaction solvent and the reactant, resulting in a molar ratio of 1:100 between ethyl laurate and methanol. As a result, there is a lot of methanol present.



1.5.4 Research Projects

Traditionally, the synthesis of ester exchange reactions has been carried out at room temperature and pressure or in supercritical methanol, usually without catalysts or with liquid catalysts. There aren't many instances of solid base-catalyzed synthesis in supercritical methanol. Additionally, the

investigation into the analysis of the reaction kinetics of solid base catalyzed reactions in supercritical methanol has not gone far enough. The development of novel solid catalyst-catalyzed ester exchange processes appropriate for high temperature and high pressure methanol environments is therefore of great interest.

It was vital to initially take into account the kinds of solid base catalysts that can be stabilized in supercritical methanol because all experiments in this study were carried out in methanol at high temperatures and pressures. Both CeO_2 and Fe_2O_3 were able to sustain a stable state at 250°C in this investigation. The reaction rates and product yields were examined after choosing the stable solid base catalyst species by contrasting the base sites and surface areas of the composite catalysts with various molar ratios. To quantitatively assess the impact of the composite solid catalysts on the diffusion process of the reactants at high temperature and high pressure methanol conditions, the findings were subjected to kinetic analysis.

2 Experimental method

2.1 Reagents

The experiments used the following reagents. Reagents for transesterification are given in Table 4, those for analysis are listed in Table 5, and those for catalyst synthesis are listed in Table 6.

Table. 4 Chemical reagents for transesterification

Name	Purity[%]	Manufacturer
Methanol	99.8	FUJIFILM Wako Pure Chemical Corporation
Ethyl Laurate	> 99.0	Tokyo chemical Industry

Table. 5 Chemical reagents for analysis (GC-FID)

Name	Purity[%]	Manufacture
Methanol	99.8	FUJIFILM Wako Pure Chemical Corporation
Methyl Laurate	> 99.0	FUJIFILM Wako Pure Chemical Corporation
Benzyl Alcohol	99.0	FUJIFILM Wako Pure Chemical Corporation

Table. 6 Chemical reagents for catalysts

Name	Purity[%]	Manufacture
Cerium(III)Nitrate Hexahydrate	> 98.5	KANTO CHEMICAL CO ,INC
Iron (III)Nitrate nonahydrate	> 99.0	KANTO CHEMICAL CO.,INC.
Citric Acid Monohydrate	> 99.5	FUJIFILM Wako Pure Chemical Corporation

2.2 Preparation of solid catalysts

The catalyst employed in this study was a complex metal oxide catalys, $\text{CeO}_2\text{-Fe}_2\text{O}_3$, which was made by citrate process.

2.2.1 Citrate Process^[48] prepare $\text{CeO}_2\text{-Fe}_2\text{O}_3$

1. Mix $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the same total mole number of Citric acid. (Molar ratio: Ce : Fe= 1:1)
2. Stir and melt at room temperature, add distilled water when it does not dissolve.
3. After complete uniformity, heat the water bath to 70°C and continue to rotate and stir.
4. After solidification, it is transferred to an electric furnace and heat treated at 170°C for 2 hours.
5. Sinter in a magnetic crucible at 550°C for 2 hours.(Citric acid breaks down into CO_2 and H_2O)
6. Cool down, obtain $\text{CeO}_2\text{-Fe}_2\text{O}_3$.

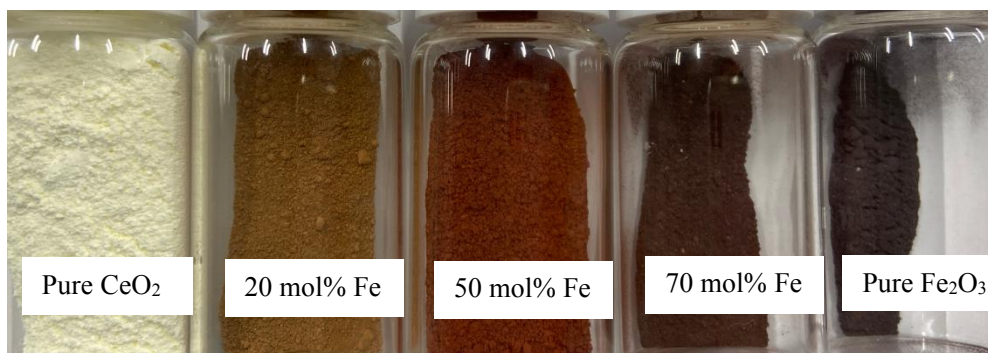


Fig. 2 Some samples of prepared catalysts

2.2.2 Advantages of Citrate Process^[49]

The Citrate Process method for the preparation of composite metal oxide catalysts has several advantages:

- a. **Simplicity and ease of use:** The citrate complexation method utilizes commonly available citric acid as a complexing agent, making the operation relatively simple and easily accessible. This method does not require complex synthesis steps or conditions, making it suitable for catalyst preparation in both laboratory and industrial settings.
- b. **Precise control:** By adjusting reaction conditions and the molar ratio of the complexing agent (citrate) to metal ions, it is possible to precisely control the composition and structure of the composite metal oxide catalyst. This method allows for the preparation of single metal oxide or multiple metal composite oxide catalysts, meeting the specific requirements of different reactions.
- c. **Enhanced catalytic performance:** The citrate complexation method effectively promotes the dispersion and uniform distribution of metal ions,

thereby improving the activity and selectivity of the composite metal oxide catalyst. The complexation of metal ions with the complexing agent (citrate) enhances the stability of the metal ions, reduces grain growth and agglomeration, and contributes to the catalyst's stability and regenerability.

d. Tunable catalyst structure: Through thermal decomposition or calcination, the structure, grain size, and pore structure of the composite metal oxide catalyst can be further controlled. This method allows for the adjustment of catalyst surface area, pore volume, and dispersion, optimizing the catalytic activity and stability of the catalyst.

e. Versatility: The citrate complexation method enables the preparation of composite metal oxide catalysts with various metal ions. By selecting different metal ions and ratios, catalysts with different compositions can be obtained, offering a wide range of potential applications. This method can be used to prepare catalysts for various applications in fields such as catalytic oxidation, reduction, hydrogenation, and redox reactions. In summary, the citrate complexation method for the preparation of composite metal oxide catalysts offers advantages such as simplicity and ease of use, precise control, enhanced catalytic performance, tunable catalyst structure, and versatility. It is a commonly used method for catalyst preparation.

2.3 Experimental procedure

The following provides a description of the tools and resources used in this study as well as the experimental techniques.

2.3.1 Features of Batch Reactor

The batch reactor is a common type of reactor used in chemical reactions. It is a closed vessel that accommodates a specific quantity of reactants and allows for a discrete and finite reaction process under controlled conditions.

Key characteristics of a batch reactor^[50] include:

1. Closed system: The batch reactor operates as a closed system, where reactants are added at the start of the reaction and removed after the reaction is complete. This allows for better control of the reaction process and reduces interactions between reactants and the environment.
2. Reaction control: Reaction conditions such as temperature, pressure, and agitation speed can be adjusted and controlled as needed in a batch

reactor. The residence time of reactants in the reactor can be extended or shortened to achieve the desired reaction extent.

3. Flexibility: Batch reactors offer high flexibility and can be used for various types of reactions. As each batch typically involves a small quantity of reactants, different reactions can be conducted, and different operations or adjustments can be made between batches. This makes batch reactors suitable for small-scale production, experimentation, and research.

4. Easy control: Due to their smaller volume, batch reactors are relatively easier to control and monitor. Addition of reactants, mixing, observation of the reaction progress, and sampling can be conducted with relative ease.

5. Temperature control: Batch reactors generally have good temperature control capability. External heating or cooling measures can be employed to adjust the reaction temperature and ensure that the reaction proceeds within the desired temperature range.

Batch reactors find wide applications in the chemical industry, particularly in cases where small-scale production, manufacturing of high-value products, or specialized reaction conditions are required. They provide a reliable and flexible approach for controlled reactions, optimization of reaction conditions, and diverse chemical product manufacturing.

2.3.2 Procedure for Batch Reactor

The usage of batch reactors is common in the chemical industry because they offer a dependable and adaptable way to carry out controlled reactions, optimize reaction conditions, and produce a variety of chemical products.

Below is a description of the processes employed.

The experiments were performed as follows.

(1) A tube made of SUS316 (1/2 inch outer diameter, 1.65 mm wall thickness, 10 cm tube length) was used as a reactor as shown in figure 3.

(2) Put the catalyst, methanol and ethyl laurate into the batch reactor in the ratio shown in table 7.

(3) The reactor's threads are greased with heat-resistant grease to prevent seizure, and the reactor lid is fastened with the required torque (50 N/m).

(4) The density of the reaction ingredient regulates the reaction pressure. Load the reactor into the heating and stirring unit after making sure the

preheating unit's temperature remains consistent at the predetermined level.

- (5) Start shaking by pressing the button on the shaking and stirring motor.
- (6) After the reactor has been heated for the allotted amount of time, remove it from the heating/stirring equipment and let it cool in water for at least five minutes.
- (7) Clean the reactor with the organic solvent methanol after removing the sample from the reactor, then add the cleaning solution to the sample.
- (8) Use a needle filter to separate the solid catalyst from the reaction solution.

Table. 7 Experiment Condition

Condition	Temperature	Pressure	Amount of $\text{CeO}_2\text{-Fe}_2\text{O}_3$	Molar ratio of Ethyl Laurate and methanol
Supercritical methanol	250 °C	10 MPa	0.05 g	1:100
Subcritical methanol	200 °C	6 MPa	0.05 g	1:100

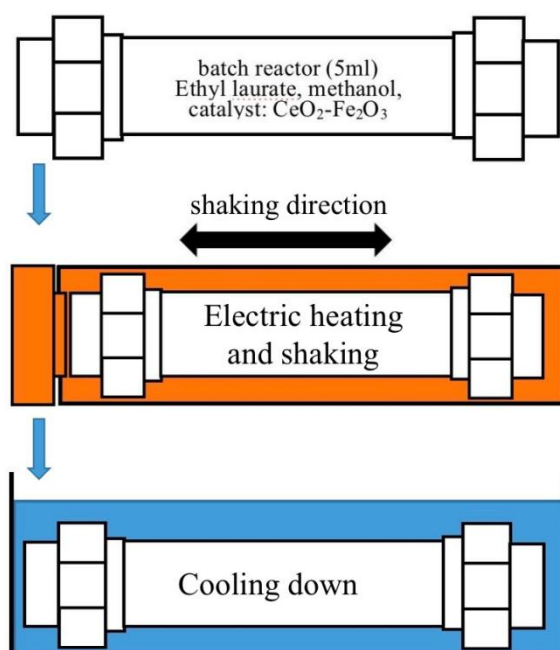


Fig. 3 The procedure of experiment

The information of the batch reactor device used for the experiment is given in table 8.

Table. 8 Chemical reagents for analysis (GC-FID)

Equipment	Shaking reactor heating and stirring unit (AKICO Corporation)	Reactor shake angle:	45°
Reactor	Intermittent reactor with 5 mL capacity	Horizontal shake frequency:	100 cycles/min.
Heat-resistant grease	MOLYKOTE 44MA	Pressure:	Saturated vapour pressure at each temperature

2.4 Analysis Method

The analyzer and analytical circumstances that were employed in this study are described in detail below.

2.4.1 Gas Chromatography with Flame Ionization Detection (GC-FID)

Gas chromatography with flame ionization detection, or GC-FID, is a method of analysis that is frequently employed. For the separation and quantitative analysis of volatile organic chemicals in samples, GC-FID combines gas chromatography (GC) and flame ionization detection (FID) techniques. During analysis, the sample is divided into many components, and these components are then detected using a flame ionization detector. The GC-FID operates on the following principles:

1. Sample injection: A gas chromatography column is used to enter the sample into the system. Depending on what is needed to separate the target chemicals, a column might be chosen.
2. Separation: The column separates the sample as it processes it. Peak separation is the result of different components moving through the column at various rates as a result of their interactions.
3. Flame ionization detection: Flame ionization detectors are used to find the separated chemicals. The chemicals are ionized in the flame to produce positive ions and electrons, and the positive ions are then gathered to provide a current signal.
4. Data processing and quantitative analysis: Recording the current signal output from the flame ionization detector will allow you to determine the compounds' peak area. Quantitative analysis of the target compound

content in the sample can be done by comparing it to reference samples with known concentrations.

GC-FID has several uses in the field of analysis, although it is most frequently used to analyze volatile organic molecules both qualitatively and quantitatively. High sensitivity, quick response times, a broad linear range, and good separation efficiency are only a few of its benefits. For the detection of volatile organic compounds, fatty acids, alcohols, ketones, ethers, aromatic hydrocarbons, and other substances, it is frequently used in environmental monitoring, food safety, pharmaceutical analysis, the petrochemical sector, and other fields.

GC-FID was used in this experiment to analyze the reactants and products in the transesterification experiment of the reactant ethyl laurate. Methanol was used as a cleaning solvent for the syringes.

This experiment used the GC-FID internal standard method, which is used to quantify target compounds in GC-FID analysis. An internal standard of known concentration (benzyl alcohol was used in this experiment) is added to the sample to be tested as a reference substance. The internal standard should have similar properties to the target compound and not react with the reactant products in a secondary way. It should also have a clear peak position in the chromatographic separation. The internal standard and the target compound are separated together through the GC column. In a FID detector, these compounds are combusted to produce a stream of ions which is measured and recorded. By comparing the peak areas or peak heights of the internal standard and the target compound, the concentration of the target compound can be determined.

The advantage of the internal standard method is that it can compensate for variability and errors in sample preparation and analysis. Through the use of internal standards, it is possible to correct for sample loss, variations in separation efficiency, and fluctuations in instrument response. This improves the accuracy and reliability of quantitative results.

The equipment used is shown in Table 9, and the columns and other conditions used are shown in Table 10.

Table.9 GC-FID Peripheral equipment

Name of equipment	Name of product	manufacturer
Ovens	GC-2014s	島津製作所
Autosamplers	AOC-20i	
System controllers	GC solution	

Table. 10 GC-FID analysis conditions

Setting item	Conditions of use
Column	TC- 1701 (medium polarity)
	I.D. 0.25 mm, 30 m, 0.25 μm
	Film thickness of liquid phase 0.25 μm
	Upper column temperature 220 $^{\circ}\text{C}$
	Manufactured by GL Science
Carrier gas He	Control mode: linear velocity
	Pressure 109 kPa
	Total flow rate 48.8 mL/min
	Column flow rate 1. 12 mL/min
	Linear velocity 29.8 cm/sec
	Purge flow rate 3.0 mL/min
	Split ratio 40 mL/min
Air inlet pressure	55 KPa
H ₂ inlet pressure	60 KPa
Make-up gas flow rate	N ₂ 45 ml/min
Vaporisation chamber temperature	250 $^{\circ}\text{C}$
Detector temperature	250 $^{\circ}\text{C}$
Detector sensitivity	1
Column temperature	100 $^{\circ}\text{C}$
Injection volume	1 μL
Retention time	Methanol 1.90 ~ 1.93 min
	Benzyl alcohol 10. 1 ~ 10.4 min
	Methyl laurate 14.5 ~ 14.8 min
	Ethyl laurate 15.5 ~ 15.8 min

2.4.2 X-Ray Diffraction (XRD)

X-Ray Diffraction or XRD is a commonly used analytical technique for studying the crystallographic properties of materials. It is based on the principle of analyzing the diffraction pattern produced when X-rays interact with a crystalline sample.

The XRD technique involves the following steps:

- a. Sample preparation: A small portion of the material of interest is ground into a fine powder and packed into a sample holder. The sample should be homogeneous and representative of the material.
- b. X-ray source: An X-ray beam, usually generated from a high-energy X-ray tube, is directed towards the sample. The X-rays have a wavelength similar to the interatomic spacing within the crystal lattice of the material.
- c. Diffraction pattern: When the X-rays strike the sample, they are diffracted by the crystal lattice planes within the material. The diffracted X-rays form a diffraction pattern, which is collected using a detector.
- d. Data collection and analysis: The diffraction pattern is recorded as a series of intensities at different angles. These intensities are related to the spacing of the crystal lattice planes and the arrangement of atoms within the material. The data can be analyzed using mathematical techniques such as the Bragg equation and Fourier transformation to determine the crystal structure, lattice parameters, phase identification, and other structural information.

In this experiment XRD was used to determine the changes in the structure of the used and unused solid base catalysts in high temperature and high pressure methanol. X-ray diffraction was performed using a SmartLab (Rigaku), which belongs to the X-ray Measurement Laboratory of the Institute of Solid State Physics, University of Tokyo. The solid catalysts measured were in powder form; Table 11 shows the main measurement conditions. X-ray diffraction (XRD) (Rigaku, SmartLab) was used to analyze the crystal structure of the synthesized particles, using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) as the X-ray source and a Bragg-Brentano diffraction system. The crystal structure was determined from the obtained XRD patterns.

Table. 11 XRD measurement conditions.

Setting Items	Conditions of use
Wire Source	Cu-K α
Voltage	40 kV
Current	30 mA
Scanning Speed	4 degrees/minute
Gap	2/3
Scanning Range	10-90 degrees
Step width	0.02 degree
Goniometer Radius	300 mm

2.4.3 TPD

TPD (Temperature Programmed Desorption) is an experimental technique used to characterize the adsorption and desorption processes on a surface. It is commonly employed to study the adsorption behavior of gas molecules on solid surfaces, particularly in the research of catalysts and adsorbent materials.

A typical TPD experiment involves the following steps:

- a. Pretreatment: The sample is initially heated to a certain temperature to remove any species that may have been adsorbed on its surface, using methods such as thermal desorption or gas flow.
- b. Adsorption: The gas molecules of interest are introduced onto the sample surface by controlling the temperature and gas pressure.
- c. Temperature ramping: The sample is gradually heated at a programmed rate, typically ranging from a few degrees to tens of degrees per minute.
- d. Desorption: As the sample temperature increases, the gas molecules adsorbed on the surface start to desorb from the sample surface.
- e. Detection: The released gas molecules during the desorption process are monitored using appropriate detection methods such as mass spectrometry or infrared spectroscopy.

By recording the changes in gas signals during the desorption process, the intensities and temperatures of desorption peaks can be obtained, providing information about the adsorption state, adsorption energy, surface active sites, and more.

The main method utilized in this experiment to identify the characteristics of the solid catalyst surface is CO₂-TPD. CO₂ (an acidic gas) was adsorbed onto the catalyst powder and its desorption as the temperature rose was measured to ascertain the amount of basic sites. The location of the peak reveals the strength of the basic site since CO₂ adsorbed on strongly basic sites desorbs at high temperatures whereas CO₂ adsorbed on weakly basic sites desorbs at low temperatures. The signal is used to calculate the peak area. The equation connecting the amount of CO₂ to the peak area can then be computed to determine the amount of CO₂ desorbed during the sample measurement.

2.4.4 Brunauer-Emmett-Teller (BET)

Brunauer-Emmett-Teller or BET is a widely used method for determining the specific surface area of porous materials, such as catalysts, adsorbents, and powders. It is based on the principle of adsorption of gas molecules onto the surface of the material.

The BET method involves the following steps:

- a. Adsorption: A gas, typically nitrogen, is adsorbed onto the surface of the material at various pressures and temperatures. The gas molecules form a monolayer on the surface.
- b. Multilayer adsorption: As the gas pressure increases, additional gas molecules are adsorbed onto the surface, forming multiple layers.
- c. Data analysis: The amount of adsorbed gas at different pressures is measured and used to construct an adsorption isotherm. The BET equation, derived from the theory of multilayer gas adsorption, is applied to analyze the isotherm data.
- d. BET surface area calculation: The BET equation allows the determination of the specific surface area by fitting the experimental data to a linear plot of the relative pressure (P/P_0) versus the quantity (P_0/VP^{-1}), where P_0 is the vapor pressure of the gas, V is the molar volume of the gas, and P is the equilibrium pressure of the gas adsorbed on the sample.

The specific surface area calculated using the BET method provides valuable information about the porosity and surface properties of materials.

In this experiment, BET was used to measure the specific surface area and pore distribution of the solid catalyst. Table 12 shows the BET measurement conditions.

Table. 12 BET Measurement conditions

Experimental procedure	Setting items	Conditions of use
Cell calibration	Adsorbate Gas	N ₂
	Thermal delay	180 s
	P0 mode	Calculate
Measurement	Sample Volume	Measure
	Thermal delay	180 s
	Adsorbate Gas	N ₂
	P0 mode	Calculate
	P0 value	760 mmHg
	Pressure tolerance	0.1 mmHg
	Equilibrium time	300 s
	Equilibrium timeout	900 s
	Reporting	Outgas time 4 h Outgas temperature 200 °C

2.5 Term Definitions

The following is an explanation of the terms used in this document.

a. Conversion (X)

The ratio of reactants to products prior to and following a reaction is known as the conversion ratio. Due to the presence of a significant amount of methanol as a solvent in this investigation, the volume of the solution was taken into consideration to be unchanged before and after the reaction. Thus, the following definition applies to the conversion (X):

$$X = \frac{C_0 - C}{C_0} = 1 - \frac{C}{C_0}$$

[C]: The concentration of ethyl laurate (mol/L)

[C₀]: The initial concentration of ethyl laurate

b. Yield (Y)

The yield is the ratio of the amount of product that was actually produced to the amount that might theoretically have been produced from the reactant input. Due to the presence of a significant amount of methanol as a solvent, it was anticipated in this investigation that the volume of the solution before and after the reaction would remain unchanged. Following is a definition of the yield (Y):

$$Y = \frac{P}{P_0}$$

[P] : The concentration of methyl laurate produced

[P₀]: Maximum theoretical amount of methyl laurate that can be produced.

c. Selectivity(S)

In a chemical process, selectivity refers to the percentage of the desired product that is produced among other products. Due to the existence of a significant amount of methanol as a solvent, it is assumed in this study that the volume of the solution does not change before and after the reaction. The following definition of selectivity (S):

$$S \equiv \frac{A_p}{A_0 - A}$$

[A_p]: The concentration of the product p

[A₀]: Initial concentration of reactants

[A]: Concentration of reactants after reaction

d. Reaction rate constant(r)

The reaction rate constant is used to describe the relationship between the rate of reaction and the concentration of reactants. It indicates the rate at which the concentration of the reactants changes per unit time. Due to the presence of a large amount of methanol as a solvent, it was assumed in this study that the volume of the solution did not change before and after the reaction. The following is the definition of the reaction rate (r):

$$r = k_B = 1 - \frac{dB}{dt}$$

[B] : Concentration of reactants

[t] : Reaction time

3 Catalyst composition analysis and stability experiments

3.1 Experimental purpose

Since the experiments for this study were done in methanol under high pressure and temperature. As a result, solid base catalysts, which is involved in this study, must be taken into account when considering solid base catalytic species that can be stable in supercritical methanol.

3.2 Experimental procedure

In this experiment, the maximum reaction temperature was 250 °C and the maximum reaction time was 90 minutes. The catalyst stability experiment was run at 250 °C for 120 minutes to see if the solid catalyst could be stable after being treated with supercritical methanol. The experiments were mostly carried out in a batch reactor. The following is the experimental procedure. The experimental conditions are shown in Table 13.

- (1) Prepare two reactors, one as a blank control group and one by adding 0.05 g of target catalyst
- (2) Add 5 mL of a homogeneous mixture of methanol and ethyl laurate (molar ratio: methanol/ethyl laurate = 100) to each of the two reactors, and label the reactor with "1" and "2" .
- (3) Set the temperature of the electrical heater to 250 °C and heat it up.
- (4) After the temperature of the electric heater has stabilized near 250 °C, the batch reactors are placed into the electric heater.
- (5) The reactors are removed and cooled with ice water after 120 minutes of feeding.
- (6) The samples are taken from the reactor once the temperature of the reactor has cooled sufficiently.
- (7) Centrifuges are used to separate the solid catalyst from the reaction solution.
- (8) Keep the reaction solution and the dry solid catalyst separate.

Table. 13 Experimental conditions for catalyst stability experiments

Setting item	experimental conditions
Reaction temperature [°C]	250
Reaction pressure [MPa]	10
Tube material	SUS316
Tube volume [cm ²]	5
Processing time [h]	2

Methanol volume [mL]	4
Catalyst mass [g].	0.05
Catalyst species studied	CeO ₂ -Fe ₂ O ₃ (Fe content:50 mol%)

3.3 XRD measurements

XRD (X-ray diffraction) is mainly used to determine the crystal structure and phase analysis of substances. XRD allows obtaining some information related to the composition of a substance, such as lattice parameters and characteristics of the crystal structure. During the XRD determination process, a preliminary judgment can be made as to whether the composition of the substance has changed by comparing the experimentally measured peak positions with data from databases or literature on known substances. If the peak positions match exactly, then the substance composition may remain unchanged. Also the intensity of the diffraction peaks in the XRD pattern is related to the structure of the crystal and lattice defects. If the composition of a substance changes, this usually leads to a change in the intensity of the peaks. Stronger peaks indicate a more complete crystal structure. If multiple crystalline phases are present in a sample, the relative content of the different phases can be inferred by analyzing the peak intensity or peak area of each phase in the XRD pattern. If the composition of the substance changes, it may lead to changes in the relative contents of different crystalline phases. In this experiment, the XRD patterns of the solid catalyst before and after the reaction were measured using 50% mol Fe as an example, as shown in the figure below. By comparing the positions and intensities of the diffraction peaks, the XRD patterns of the catalysts before and after the reaction were almost completely overlapped without obvious changes. This confirms that the material structure and crystal structure of the catalyst are very likely to remain stable after 120 min of reaction in supercritical methanol. The XRD profiles of CeO₂-Fe₂O₃ 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 CeO₂-Fe₂O₃ is stable at high temperature and pressure.

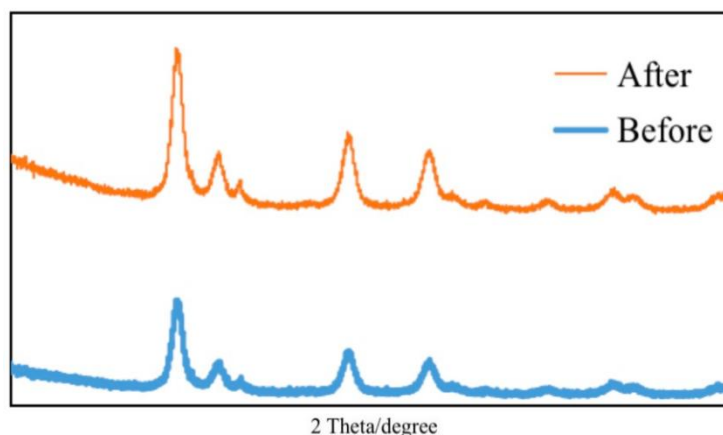


Fig. 4 The XRD profiles of 50 mol% Fe before and after the reaction

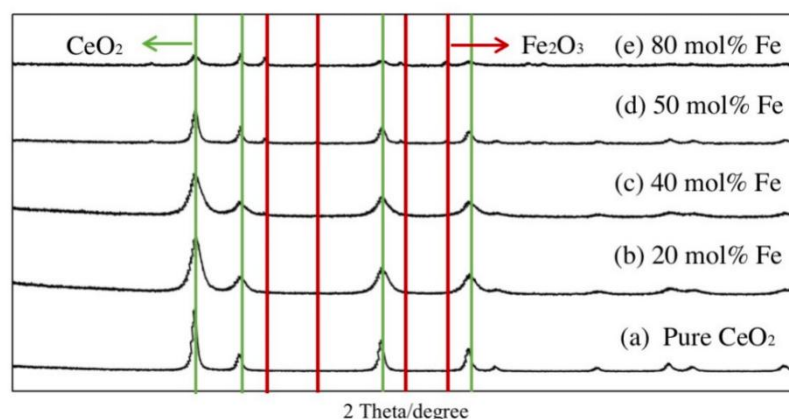


Fig. 5 XRD profiles of $\text{CeO}_2\text{-Fe}_2\text{O}_3$ samples, Fe content: (a) 0 mol%, (b) 20 mol%, (c) 40 mol%, (d) 50 mol%, (e) 80 mol% (Red line: peak of Fe_2O_3 Green line: peak of CeO_2)

Fig. 5 shows the XRD profiles of the $\text{CeO}_2\text{-Fe}_2\text{O}_3$ peaks, it can correspond to CeO_2 and Fe_2O_3 and 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.

3.4 CO_2 -TPD and BET

TPD of CO_2 adsorbed on the $\text{CeO}_2\text{-Fe}_2\text{O}_3$ was measured to characterize the basicity (Fig. 6). 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 Fe₂O₃ to CeO₂ alters the amount of CO₂ desorption up to 600 °C. Fig.7 shows the number of basic sites and specific surface area of CeO₂-Fe₂O₃ samples. The number of basic sites reaches a maximum at 40-60mol% Fe. The specific surface area also varies with Fe content. 50 mol% Fe mixed catalysts have a higher surface area than pure CeO₂.

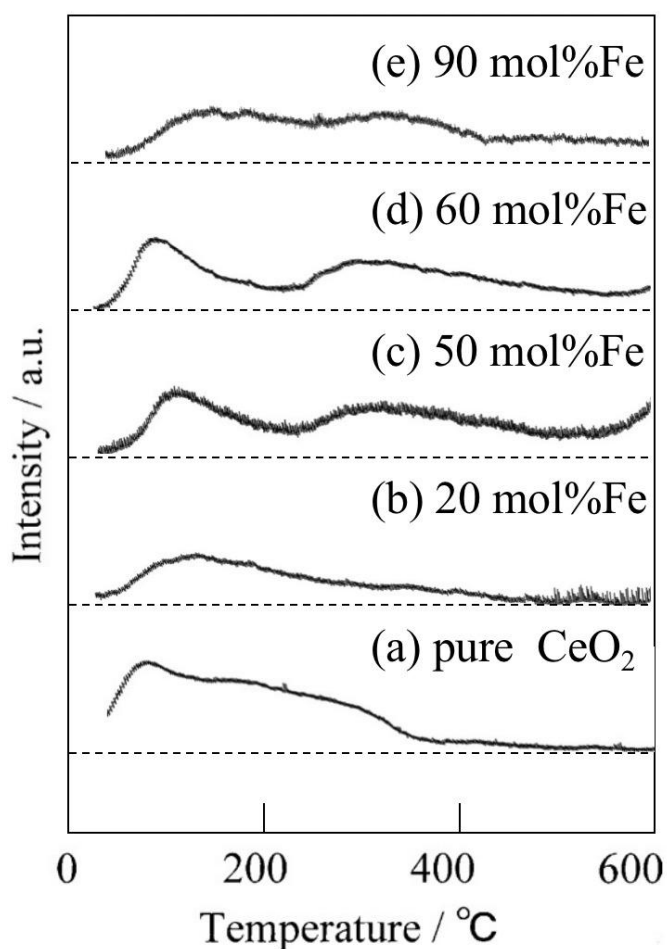


Fig.6 TPD profiles of CO₂ adsorbed on CeO₂-Fe₂O₃ catalysts with different Fe contents: (a) Fe content: 0 mol%, (b) 20 mol%,(c) 50 mol%, (d) 60 mol%, (e) 90 mol%

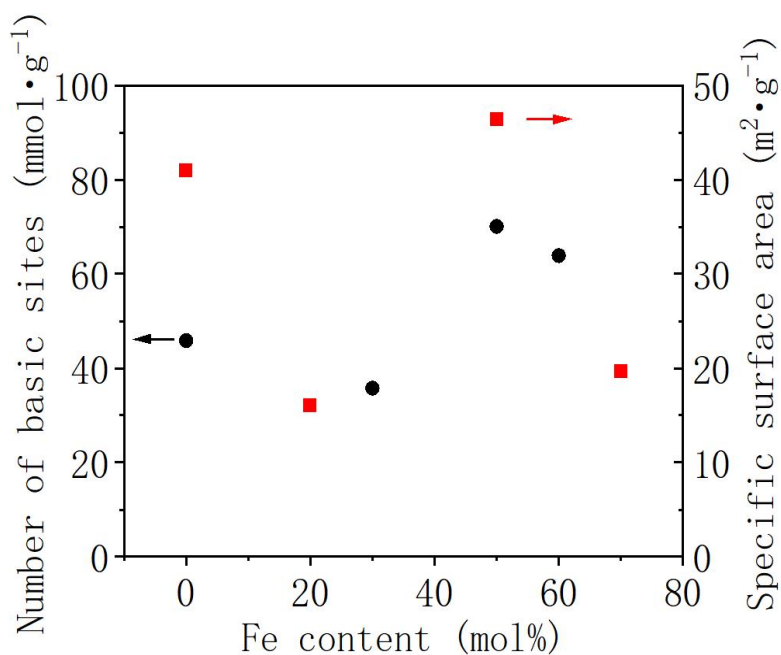


Fig. 7 Changes in number of basic sites and specific surface area of $\text{CeO}_2\text{-Fe}_2\text{O}_3$

3.5 GC-FID

GC-FID profiles can provide information about the appearance time of the peaks, the shape of the peaks and the peak area of the peaks of different components in the sample. In this experiment, GC-FID was mainly used to analyze the conversion rate of reactants and the generation rate of products. By observing the appearance time of different peaks in the GC-FID profile. If the time of peak appearance does not coincide with the expected time of occurrence of reaction or dissolution, it may mean that the component is not reacting or not dissolving. Also if the shape of the peaks does not change and matches the expected peak shape, it can imply that the component is not reacting or not dissolving.

The figure 8 shows the GC-FID profile measured after the catalyst stability experiment using 50% mol Fe as an example. It can be observed through the graph that there are no miscellaneous peaks other than the initial corresponding product and reactant peak areas. Basically, it can be stated that the catalyst does not produce other by-products with reactants under supercritical methanol conditions and is also insoluble.

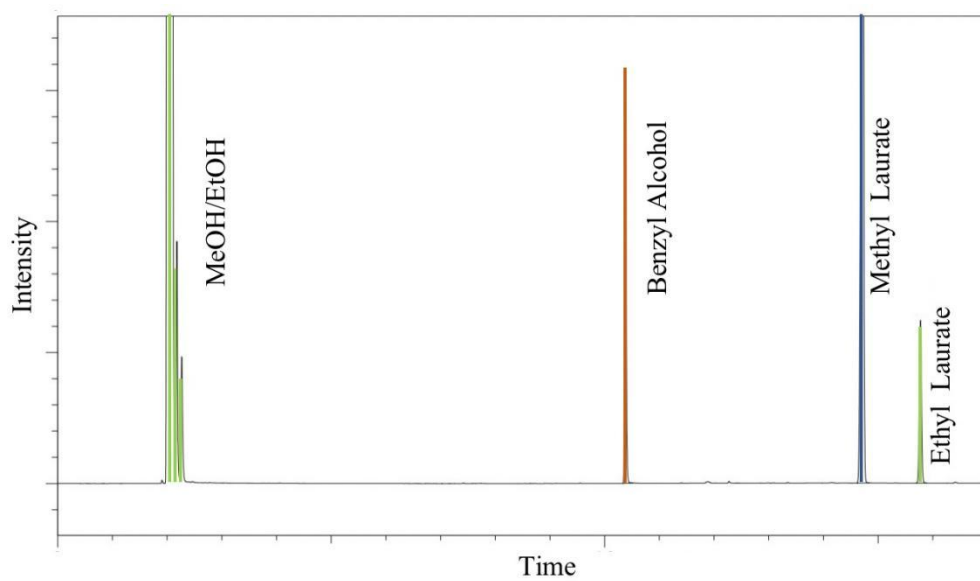


Fig. 8 GC-FID profiles of reaction(50 mol%Fe)

4 Catalytic transterification of ethyl laurate

4.1 Qualitative analysis of products

Analyzing the GC-FID spectrum of the transesterification reaction of ethyl laurate and methanol catalyzed by the catalyst measured in this experiment, it can be seen (as shown in Fig. 7) that several peaks correspond to methanol, ethanol, methyl laurate, ethyl laurate, and there are no other impurity peaks. And it can be determined by the catalyst stability experiment that the prepared catalyst does not dissolve without side reaction, so it can be determined that there are no other impurities except the reactants and products.

4.2 Quantitative analysis of products

During the quantitative analysis, the products were quantified by the internal standard method of GC-FID in the following steps:

- a. Benzyl alcohol was chosen as the standard substance in the internal standard method because has similar properties to methyl and ethyl laurate and does not react with them in secondary reactions. It also has a large difference in boiling point (benzyl alcohol: 207.5 °C , methyl laurate: 262 °C , ethyl laurate: 269 °C) and has a well-defined peak position in the chromatographic separation.
- b. A known concentration of benzyl alcohol was added to five sample vials as a reference substance and each was labeled with a number from 1-5.
- c. A known mixture of ethyl laurate and methyl laurate in different concentration gradients was added to each of the sample vials numbered 1-5 and diluted with a quantitative amount of methanol.
- d. The five sample compounds made were separated together by passing them through a gas chromatography column. In the FID detector, these compounds are combusted to produce a stream of ions, which is measured and recorded.
- e. The concentration of the target compound can be determined by comparing the peak areas or peak heights of the internal standard and the target compound. The concentration and peak area in the five sample vials are used to obtain a linear relationship between methyl laurate and benzyl alcohol and a linear relationship between ethyl laurate and benzyl

alcohol.

f. The concentration and peak area in the five sample vials is used to obtain. This is also known as the standard curve.

g. The mixture obtained after the reaction was diluted and treated with methanol, and a quantitative amount of the internal standard substance benzyl alcohol was added.

h. The peak areas of the different peaks were measured by GC-FID after filtration through syringe filter. The concentrations of the different substances in the mixture after reaction were obtained by taking the standard curve.

The formula for calculating the concentration of the internal standard method is given below :

$$\frac{A_s}{C_s} = F \times \frac{A_t}{C_t}$$

[C_t] Target compound concentration

[A_t] Target compound peak area

[C_s] Internal standard compound concentration

[A_s] Internal standard compound peak area

[F] Coefficient of standard curve

By measuring the peak area or peak height of the target compound and the internal standard, and using the concentration of the internal standard, the concentration of the target compound can be calculated. The internal standard method improves the accuracy and reliability of quantitative results by eliminating variability during sample preparation and analysis.

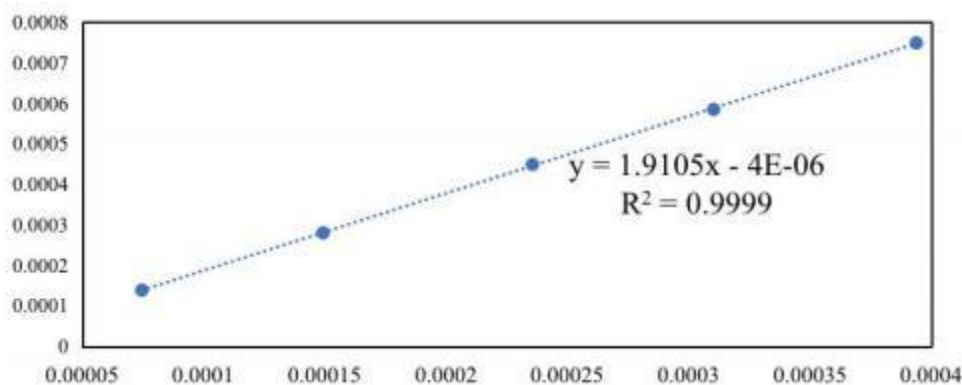


Fig . 9 The standard curve by internal standard method.

4.3 Experiments to study the effect of CeO₂-Fe₂O₃ and residence time on conversion and yield in supercritical methanol

In this study, the experiments were first carried out at supercritical methanol conditions (250 °C 10 MPa) and subcritical methanol conditions (200 °C , 6 MPa) for 30 min, 60 min, and 90 min, respectively, using 50% mol Fe as an example. The experimental steps are as follows :

- a. Since the methanol content was much larger than the other substances, a mixed solution was prepared according to the molar ratio: methanol/ethyl laurate = 100 according to 200 °C , 6 MPa or 250 °C , 10 MPa corresponding to different methanol densities, respectively.
- b. Weigh three portions of 0.05 g of the prepared catalyst and add them into three reaction tubes.
- c. A homogeneous mixture of 5 ml of methanol and ethyl laurate was added to each of the three reaction tubes and the weight of the liquid was weighed. The three reaction tubes were then labeled "1", "2" and "3".
- d. Set the temperature of the electrical heated reactor to 250 °C /200 °C and heat it up.
- e. After the temperature of the electric heater has stabilized near 250 °C /200 °C , the batch reactors are placed into the electric heater.
- f. The reactors are removed and cooled with ice water after 30/60/90 minutes of feeding.
- g. The samples are taken from the reactor once the temperature of the reactor has cooled sufficiently.
- h. Centrifuges are used to separate the solid catalyst from the reaction solution.
- i. Keep the reaction solution and the dry solid catalyst separate.

Table 14 Experimental conditions for catalytic transesterification under supercritical and subcritical methanol

Setting item	Setting value	
Temperature	250 °C	200 °C
Pressure	10 MPa	6 MPa
Solid base catalyst type	CeO ₂ -Fe ₂ O ₃ (Fe content: 0%- 100%)	
Catalyst weight	0.05 g	
Reactant solution weight	4 g	

The yields and conversions are shown below.

In supercritical methanol, at 250 °C, reactions with and without catalyst were investigated. Fig.10 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.

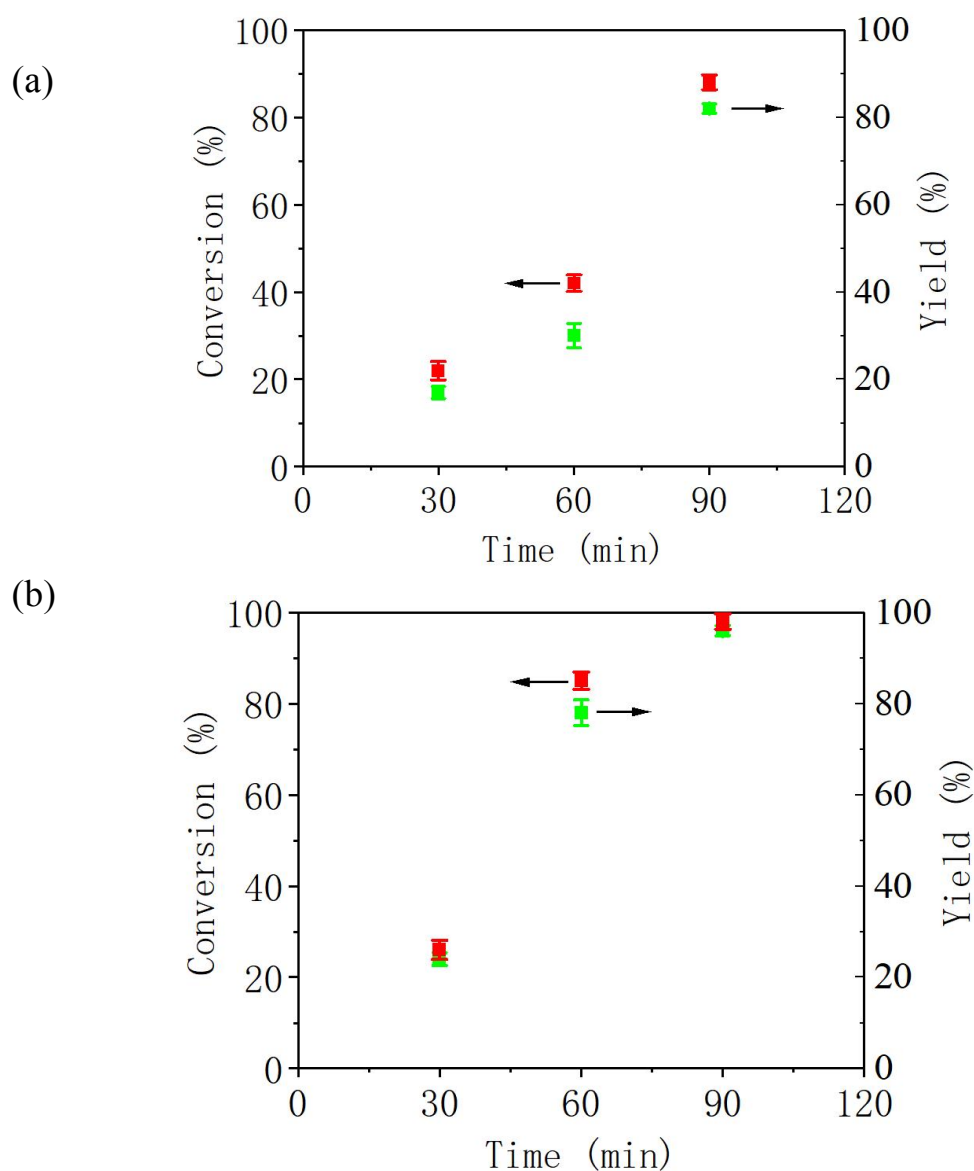
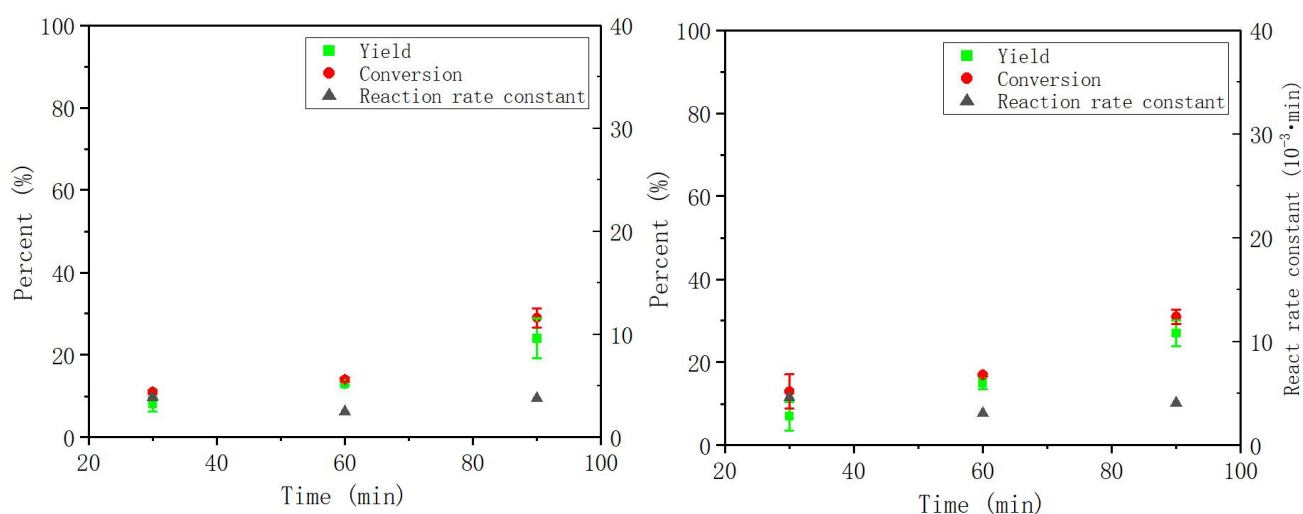


Fig. 10 Yield and conversion VS.Time (a) no catalyst (b) 50 mol% Fe (0.2wt%) (●) conversion (■)Yield

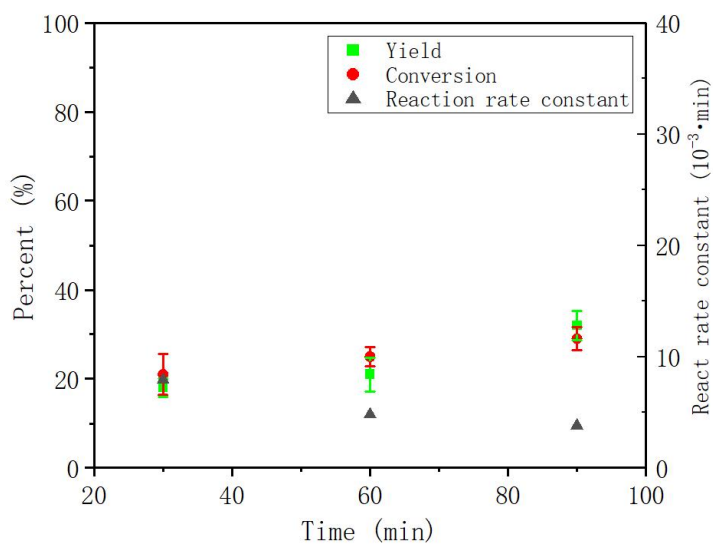
4.4 Experiments to study the effect of different Fe content and residence time on conversion and yield in subcritical methanol

Eleven mixed metal oxide catalysts ranging from 0% mol Fe to 100% mol Fe content were prepared in this experiment. The experimental steps were the same as in 4.3. 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 mol% Fe catalysts on ethyl laurate and the control group were measured at 200°C, 6 MPa, respectively. Their conversions and reaction rate constant are shown in Fig. 11 and Fig. 12. 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. 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.

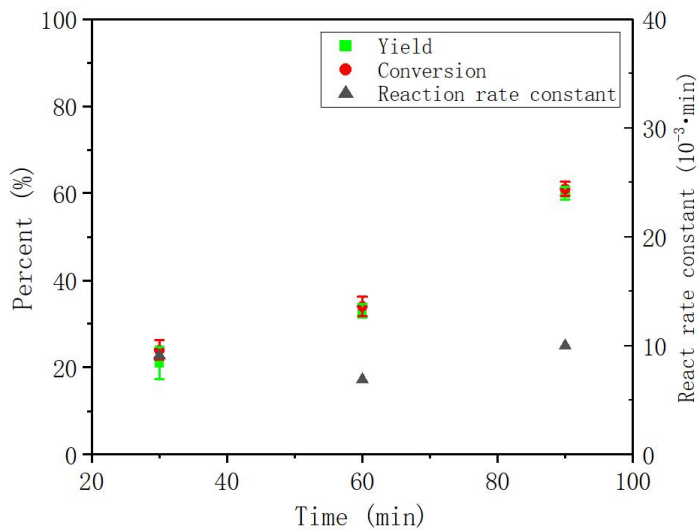


(a) 10 mol% Fe

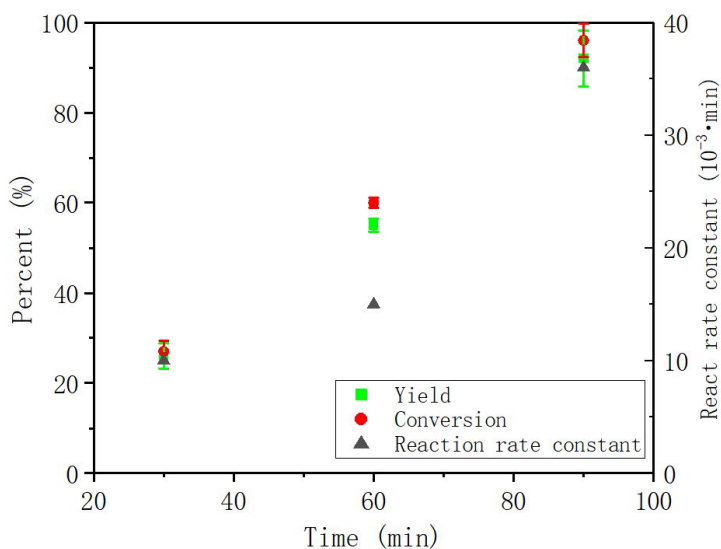
(b) 20 mol% Fe



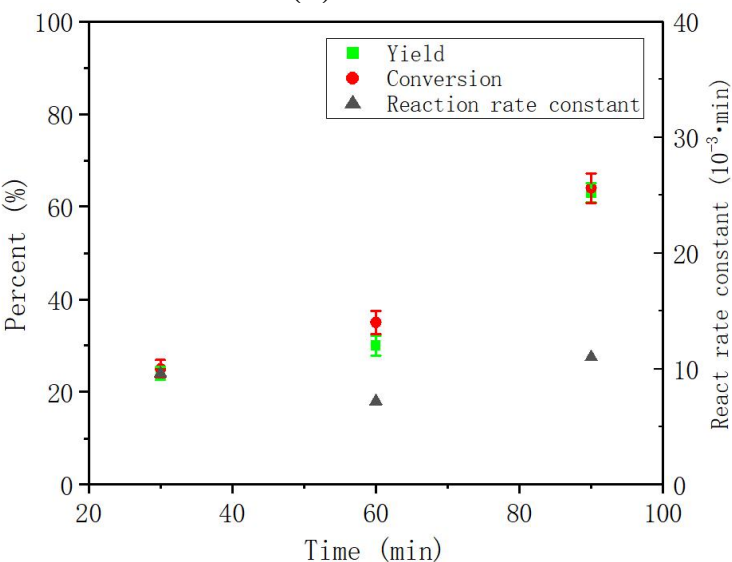
(b) 30 mol% Fe



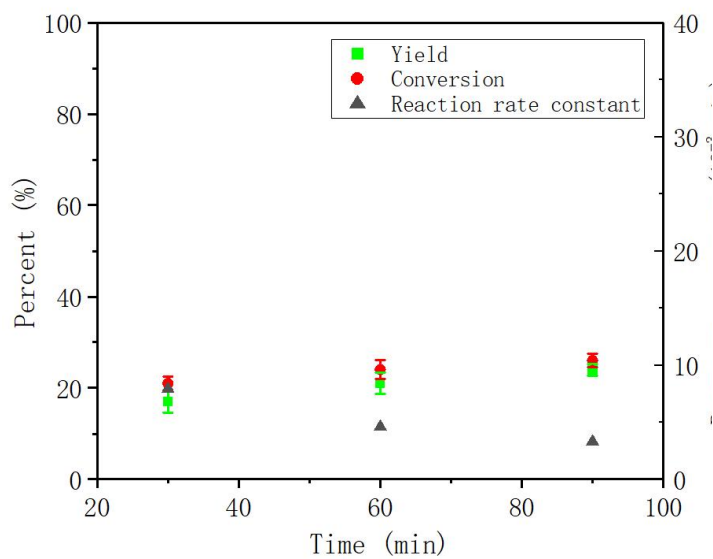
(d) 40 mol% Fe



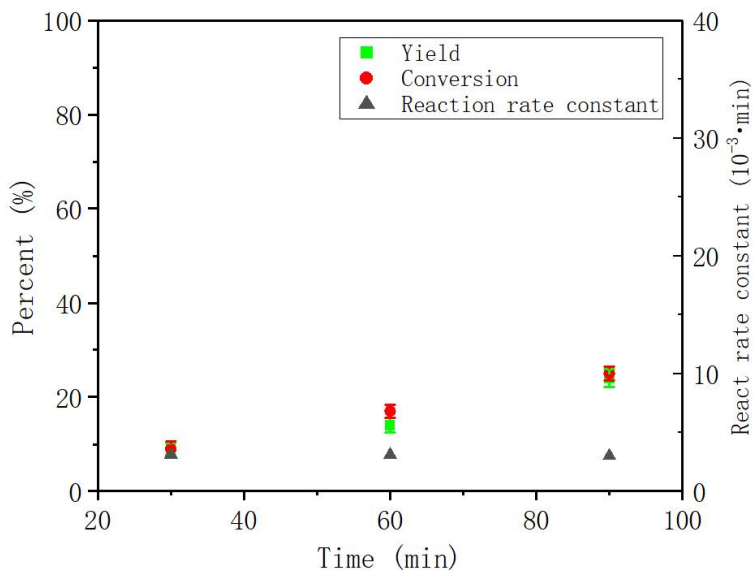
(e) 50 mol% Fe



(f) 60 mol% Fe



(g) 70 mol% Fe



(h) 80 mol% Fe

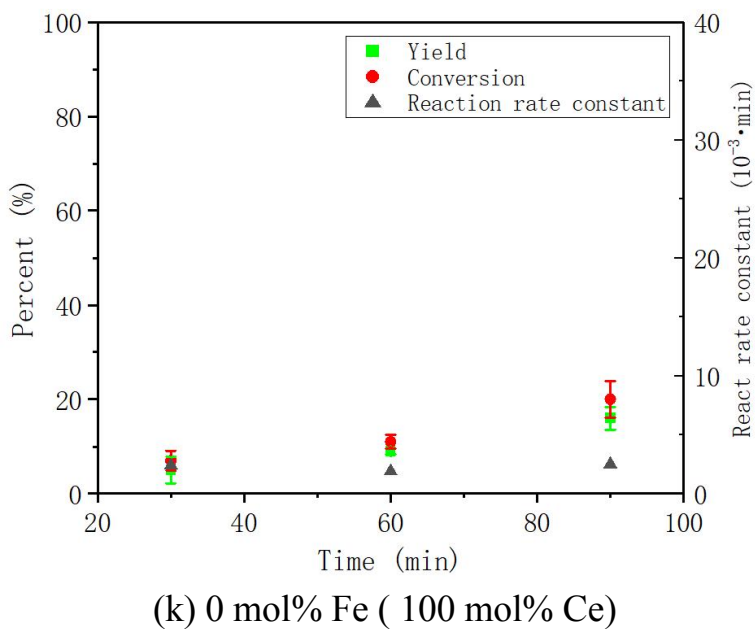
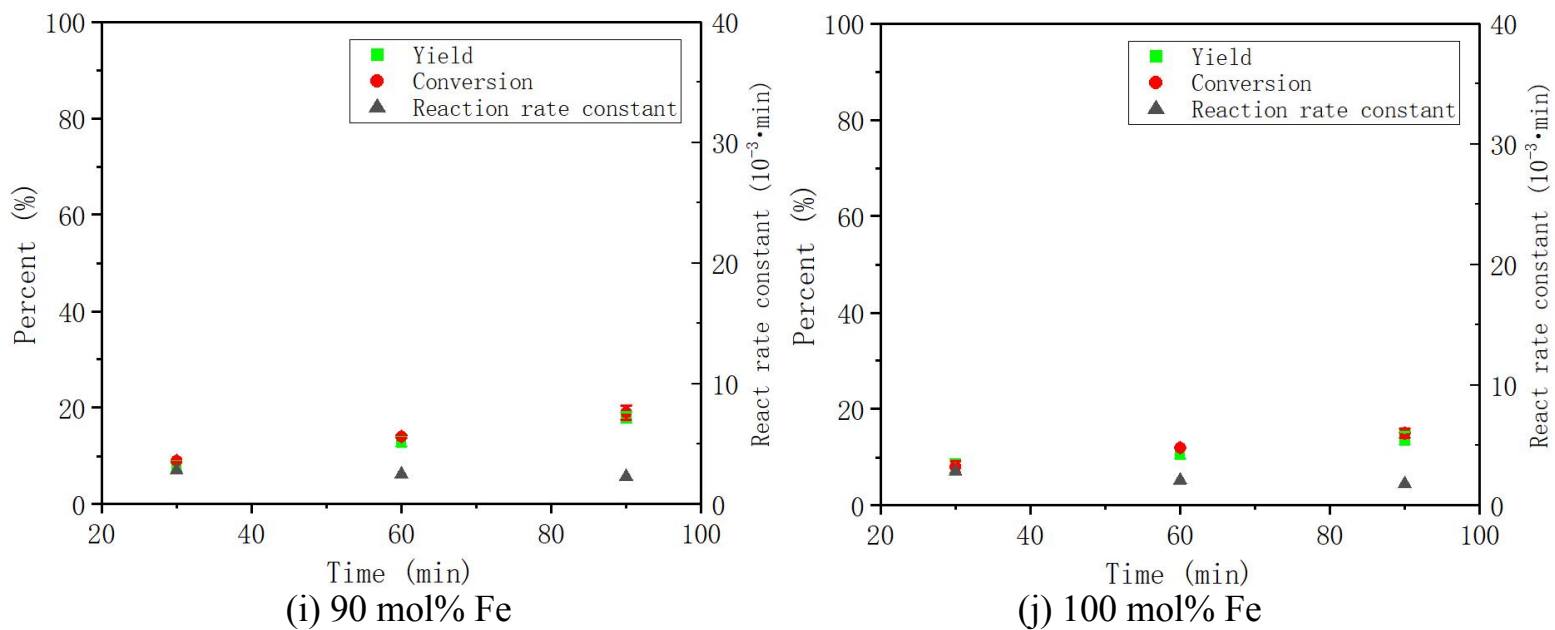
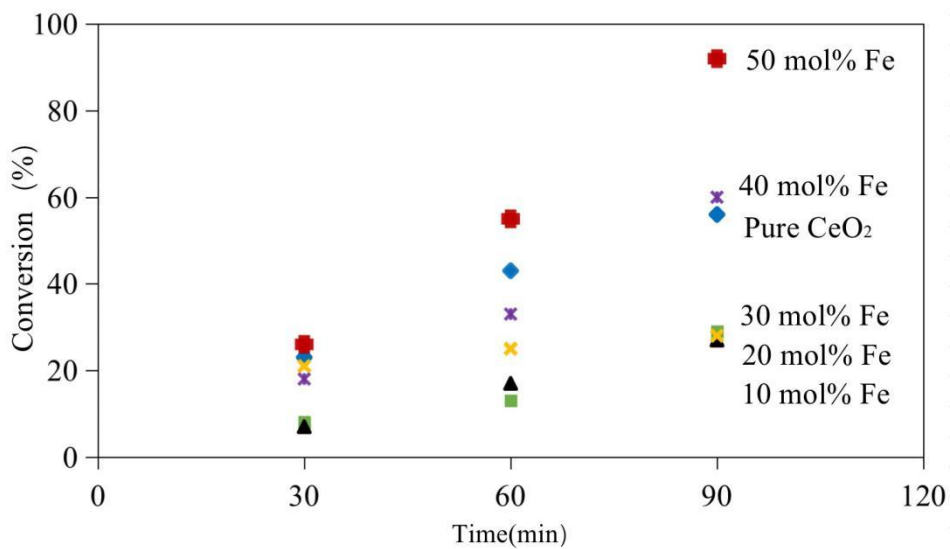


Fig. 11 Yield, conversion and reaction rate constant VS. Time

(a)



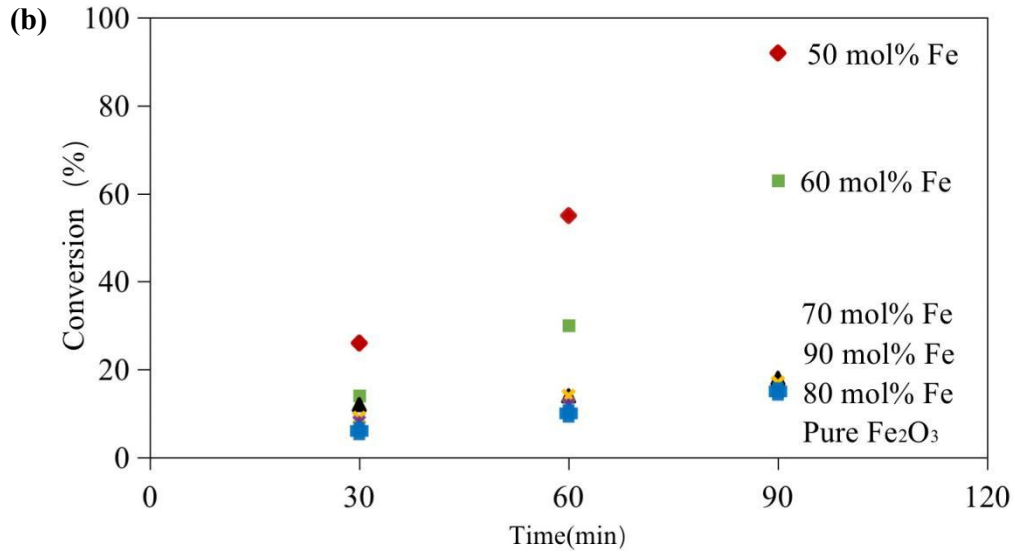


Fig. 12 Average conversion VS. Time with different Fe content (a) 0-50 mol% Fe (b)50- 100mol%Fe

4.5 Experiments to study the rate of reaction for different Fe contents

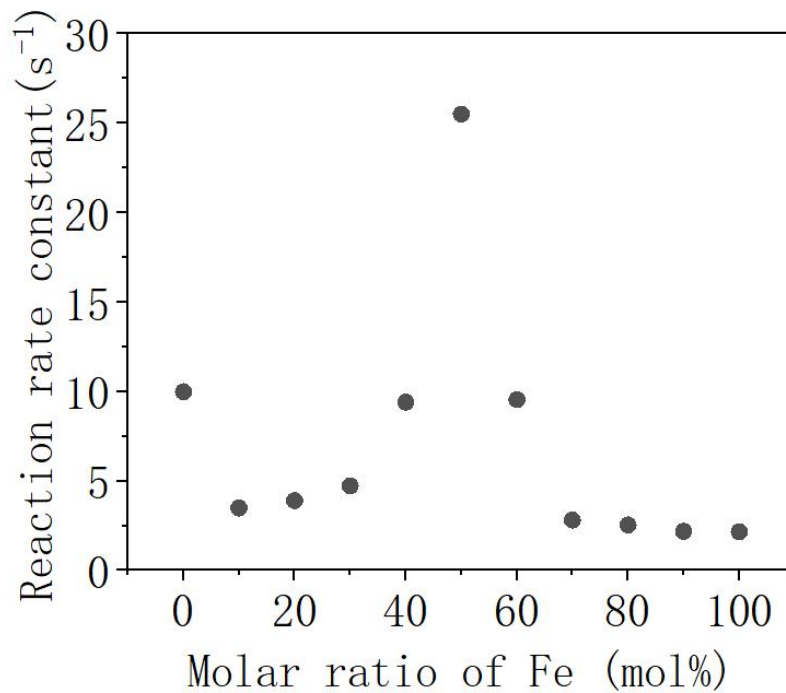


Fig. 13 Reaction rate constant VS. different Fe content

The reaction formula in this experiment is a first-order chemical reaction, and its reaction rate equation can be expressed as:

$$\text{Differential form: } r = -dc/dt = kc$$

$$\text{Integral form: } \ln(a/c) = kt$$

In the above formula, a is the concentration of the reactant at the beginning of the reaction, c is the concentration of the reactant at time t , k is the rate constant, and the unit is the negative power of the time unit.

Fig. 13 is first-order kinetic rate constant with different Fe content. From the results of reaction rate constant, the basic sites are most abundant when the Fe content is 50%, followed by 40%, 60% and 0%, which also corresponds exactly to the magnitude of the conversion and reaction rate constant of the catalytic transesterification under subcritical methanol.

4.6 Experiment to study the effect of temperature

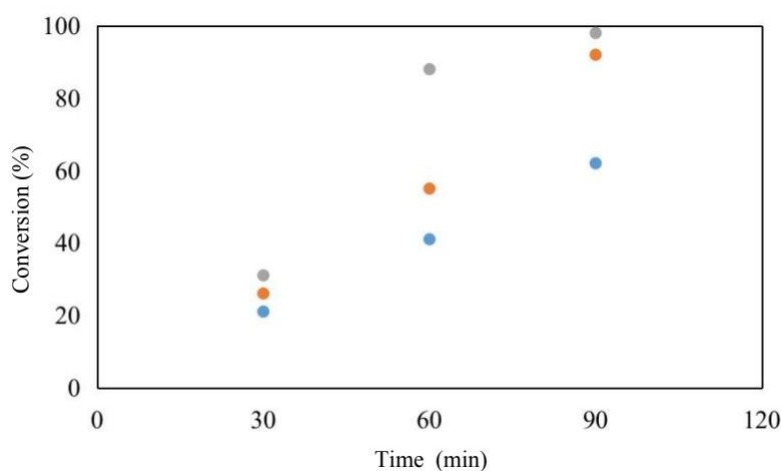


Fig. 13 Time dependence of conversion (Fe content : 50 mol%)
● 180°C ● 200°C ● 250°C

Temperature is one of the important factors in transesterification reactions, and this experiment was conducted to determine the catalytic efficiency of the transesterification reaction regarding the same catalyst at three different temperatures.

As the temperature increases, the catalytic effect of the same catalyst at the same time increases significantly. Temperature is one of the major factors in catalyzed transesterification reactions. The addition of catalysts compensates to some extent for the reduction in conversion due to lower temperatures.

5 Comparison and discussion with solid metal oxide catalysis in past subcritical methanol

5.1 Catalytic principle of metal oxides under high temperature and high pressure methanol

When a solid basic catalyst is added to a solution of reactants, there is a boundary film near the surface of the catalyst particles. The first step in a solid catalyzed reaction is the diffusion of reactants to the surface of the catalyst. The reactants first pass through the boundary film from the fluid body to the catalyst surface. Subsequently, they diffuse into the pores on the catalyst surface. High temperature and high pressure methanol is less viscous and more diffusive. As a result, methanol molecules, accompanied by reactants, pass through the boundary membrane and reach the basic sites very quickly. Therefore, solid base-catalyzed reactions in high-temperature, high-pressure methanol have faster reaction rates than solid base-catalyzed reactions in methanol at room temperature.

5.2 Single metal oxide catalysts in transesterification reactions

The early studies on heterogeneously catalyzed transesterification were focused on the catalysis by single metal oxides.

Low Temperature: Generally speaking, single-compound solid bases are relatively ineffective at transesterifying oils and fats. In their investigation of the MgO-catalyzed transesterification of rapeseed oil with methanol at the methanol boiling point (64.7 °C), a ratio of 75:1, a reaction time of 22 hours, and a catalyst dosage of 10 weight percent, Leclereq et al. discovered that the conversion rate of methyl esters of fatty acids was only 64%.

Subcritical Methanol: For the esterification of glycerol with fatty acid methyl esters (FAME) at 220 °C, Bancquart compared the base-catalyzed activity of single metal oxides such La₂O₃, MgO, CaO, and ZnO [36]. The authors came to the conclusion that the basicity of the oxides, particularly the basicity of the strongly basic sites, directly affects the pace of reactivity of single metal oxides. As a result, the order of activity is as follows: La₂O₃ > MgO > ZnO > CeO₂.

It can be seen that the catalytic performance of single metal oxide catalysts does not perform well at room temperature. Under subcritical methanol conditions, there are few types of metal oxides with good

catalytic performance, so the goal is to change the composition of the catalyst itself to achieve the purpose of enriching the catalyst types and improving the catalytic performance.

In my experiment, CeO₂ with relatively weak basicity as determined by Bancquart et al. was used and the basicity property of CeO₂ were improved by changing the composition of the catalyst by lowering the temperature from 220°C.

5.3 Composite metal oxide catalysts for transesterification reactions

Due to interactions between the molecules of various substances, complexes of metal ions and loaded solid base catalysts can produce particular specialized structures or superbases. When compared to single compounds, these complexes exhibit enhanced solid base catalytic activity.

In the study by Chawalit et al., the transesterification process between palm kernel oil and alcohols was catalyzed by using calcium (Ca) and zinc (Zn) mixed oxides as a heterogeneous base catalyst. We looked at the selectivity and catalytic activity of calcium and zinc mixed oxides. At 60 °C, catalyst dose of 10 wt%, methanol/oil molar ratio of 30, reaction time of 3 hours, and a Ca/Zn ratio of 0.25 for the CaO-ZnO catalyst, the methyl ester concentration may reach >94%. The transesterification of palm, soybean, and sunflower oils can also be done using the mixed oxide. In comparison to pure CaO and ZnO, the mixed oxide has a comparatively tiny particle size and a large surface area.

Single metal oxides may benefit from the addition of mixed metal oxides in terms of stability. Al₂O₃-SnO and Al₂O₃-ZnO catalysts were produced by Macedo et al. [44] and their efficacy was evaluated. After 4 hours, 80% of the biodiesel production was generated from soybean oil using catalysts at a rate of 5 wt% at 60°C.

A-B-O type metal oxides were investigated by Kawashima et al. [46], where A is an alkaline-earth metal (Ca, Ba, Mg), alkaline metal, or rare earth metal (La), and B is a transition metal (Ti, Mn, Fe, Zr, Ce). The catalysts were created by calcining a ball-milled mixture of transition metal (B) oxide and alkaline metal (A) carbonate at a high temperature. The high-temperature calcination produced catalysts with extremely low specific surface areas (0.7–4.9 m²/g). In terms of Hammett basicity (H₋), catalysts from the Ca series, such as CaMnO₃, Ca₂Fe₂O₅, CaZrO₃, and

CaCeO_3 , exhibited base strengths that ranged from 7.2 to 9.3, whereas those from the Ba, Mg, and La series had the lowest base strengths (6.8). The transesterification reaction, in which the Ca series catalysts had strong catalytic activity, was consistent with these findings. Particularly, CaZrO_3 and CaO-CeO_2 catalysts demonstrated stable methyl ester yields of 80% at 60 °C with an oil/methanol ratio of 6:1, and this activity was sustained after 5-7 reaction iterations.

As was mentioned in the preceding section, the mild transesterification activities of single metal oxides such CaO. Due to its low mechanical strength, some CaO was converted into a suspensoid in some applications, which made it difficult to separate the catalyst from the biodiesel products. In an effort to address this issue, Yan et al. ^[47] impregnated CaO on metal oxide carriers. Basic oxide MgO, neutral oxide SiO_2 , acidic oxide Al_2O_3 , and zeolite HY were used as support materials and the best result was obtained with CaO/MgO, in which case the conversion of rapeseed oil reached 92% at 64.5 °C . After four reaction iterations, there was a noticeable decrease in activity, which the authors attributed to the active site being blocked by adsorbed intermediates or product species, such as diglyceride, monoglyceride, and glycerin, as well as contamination from O_2 , H_2O , and CO_2 in the air during the catalyst filtering process. Through high-temperature treatment, the activity was almost brought back to its original level, although the operation also required an additional dosage of calcium precursor.

The past experiments show that the studies of Chawalit et al. and Macedo et al. had low experimental temperatures but high catalyst dosages of 10 wt% and 5 wt% and long reaction times of 3-4 h. The experimental results of Kawashima et al. showed that CeO_2 , as a transition metal oxide, could substantially improve the catalytic performance of CaO in alkaline catalytic applications, but the reactant yield was around 80%, which still did not achieve the fullest possible conversion. Yan et al.'s experiments were designed to improve the stability of single metal oxides, and it was demonstrated by the impregnation method that the selection of appropriate mixed metal oxides resulted in better stability and catalytic performance compared to single metal oxides.

In this experiment, the stability and catalytic performance of the metal oxides were improved by adjusting the ratio of the composite metal

oxide catalysts. Maximizing basicity by testing different ratios of two metals that are not highly basic.

6. 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.

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