Catalytic Pyrolysis of Biodiesel Surrogate over HZSM-5 Zeolite Catalyst

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To obtain insight into the catalytic reaction mechanism of biodiesels over ZSM-5 zeolites, the pyrolysis and catalytic pyrolysis of methyl butanoate (MB), a biodiesel surrogate, with H-type ZSM-5 (HZSM-5) were performed in a flow reactor under atmospheric pressure. The pyrolysis products were identified and quantified using gas chromatography-mass spectrometry (GC-MS). Kinetic modelling and experimental results revealed that H-atom abstraction in the gas phase was the primary pathway for MB decomposition during pyrolysis, but dissociating to ketene and methanol over HZSM-5 was the primary pathway for MB consumption during catalytic pyrolysis. The initial decomposition temperature of MB was reduced by approximately 300 K over HZSM-5 compared to that for the uncatalyzed reaction. In addition, the apparent activation energies of MB under catalytic pyrolysis and homogeneous pyrolysis conditions were obtained using the Arrhenius equation. The significantly reduced apparent activation energy confirmed the catalytic performance of HZSM-5 for MB pyrolysis. The activation temperature may also affect some catalytic properties of HZSM-5. Overall, this study can be used to guide subsequent catalytic combustion for practical biodiesel fuels.

Key words: Methyl butanoate, HZSM-5, Catalytic pyrolysis, Reaction kinetics, Biodiesels

I. INTRODUCTION

Biodiesel is widely used as a substitute for fossil fuels due to its environmental friendliness and renewability [1, 2]. Representative biodiesel is composed of C\textsubscript{14}–C\textsubscript{22} long-chain fatty acid methyl esters (FAME), obtained by converting biomass via transesterification [3–5]. However, due to the influence of high temperatures and incomplete reactions inside engines, the biodiesel combustion generates pollutants such as CO, nitrogen oxide (NO\textsubscript{x}), and volatile organic compounds (VOCs) [6, 7]. Previous studies have shown that NO\textsubscript{x} emission may increase during biodiesel combustion compared to the case of regular diesel fuel [8, 9].

Catalytic combustion technology is a promising method to reduce pollution emissions [10]. Compared to post-treatment methods, such as selective catalytic reduction (SCR) [11], catalytic combustion can reduce the generation of pollutants by completely oxidizing the fuel at low temperatures [12, 13]. For example, hydrocarbons from the incomplete combustion of fuels and NO\textsubscript{x} generated during high-temperature combustion [14, 15] can be effectively reduced via low-temperature catalytic combustion. It should be noted that catalysts can promote the complete oxidation of fuel at low temperatures, but must maintain long-term activity and structural stability at relatively high temperatures [16]. Therefore, catalysts with high-temperature stability and catalytic activity, including noble metals and non-noble metal oxides, have often been used as catalysts or catalyst carriers for catalytic combustion [12, 17, 18].

Pd is a precious metal and an excellent catalyst for the catalytic combustion of methane [19], and can be used in gas turbines to test the actual performance of methane catalytic combustion process [20, 21]. Besides Pd, Pt and Rh are ideal catalysts for application in the combustion of typical fuels like methane and propane [22–24]. However, noble metals are not suitable catalysts for widespread applications for fuel combustion due to their high cost. Instead, economical single and mixed metal oxides are better choices [12, 25]. Hexaaluminate is a promising catalyst for the catalytic combustion of methane and natural gas [18, 26] and its catalytic activity can be improved by doping. However, its relatively low specific surface area may limit any fur-
Zeolites are widely used as mixed metal oxides with a porous structure and relatively high specific surface area [28]. The synthetic zeolite, ZSM-5, is a widely studied zeolite catalyst [29, 30] due to its good thermal stability, hydrothermal stability, and hydrophobicity [31–33]. These properties allow it to be used as a catalyst or a catalyst supporter in catalytic combustion and pyrolysis processes [34, 35]. Previous studies have shown that ZSM-5 can facilitate ester decomposition at low temperatures [36, 37].

Generally, catalytic combustion experiments represent a reasonable approach to study the oxidation of fuel over catalysts. However, from the existing reaction mechanisms of catalytic combustion, the proportion of anaerobic reactions on the surface of catalysts is considerable [38–40], and the relatively rapid oxidation reaction complicates the examination of anaerobic pathways. Moreover, a singular catalytic combustion experiment cannot often reveal the catalytic oxidation mechanism experimentally.

According to classical catalytic oxidation models [17, 41], a point of controversy is how the oxygen interacts with the fuel molecule over the catalyst. In this context, the anaerobic catalytic pyrolysis of fuels is an important reference and can act as a supplement to catalytic combustion. In addition, catalytic pyrolysis is considered to be “special” catalytic combustion with an equivalent ratio of infinity, which is a boundary condition.

To explore the reaction mechanism of biodiesel on the surface of ZSM-5, catalytic pyrolysis of methyl butanoate (MB) over unmodified H-type ZSM-5 (HZSM-5) was performed in a flow tube reactor. These investigations will be meaningful for determining the catalytic combustion mechanism of biodiesel and subsequent catalyst modification strategies. HZSM-5 was selected to examine the general catalytic behaviour of the porous framework of ZSM-5 towards the methyl ester. Although the application of HZSM-5 has been reported in many previous studies [42–45], little research has focused on the catalytic decomposition of methyl esters. MB, as a methyl ester, is an ideal biodiesel surrogate and is chosen herein because it retains most of the properties of biodiesel, including fast isomerisation reactions and negative temperature coefficient behaviour [46, 47]. The study aims to explore the differences between the surface reaction of methyl esters over the catalyst and the homogeneous reaction of methyl esters in the gas phase by measuring variation of product fractions and reaction temperatures. The relatively short carbon chain of MB will likely yield manageable products and reaction pathways [48, 49], leading to simplification and a better perspective. The reaction mechanism of MB over HZSM-5 will be explored, and the results will be meaningful to larger methyl esters over ZSM-5 catalyst.

II. EXPERIMENTS

The detailed schematic of the pyrolysis apparatus is provided in FIG. 1. The experimental setup for catalytic pyrolysis consists of three main parts: a sample injection system, pyrolysis chamber, and detection system (gas chromatography-mass spectrometry, GC-MS). To be more detailed, the liquid sample injection system features a chromatographic pump to control the flow rate and an electrically heated vaporiser to vaporise the liquid samples. Furthermore, a flow controller with a 300 SCCM (standard cubic centimeter per minute) range was used for the gas samples. These two parts were connected with the vaporiser to mix the gas and vaporise liquid. Afterward, the premixed gas is sent to

FIG. 1 The schematic of catalytic pyrolysis apparatus with GC-MS.
The pyrolysis chamber was composed of a tube furnace, with temperature that can be controlled from 298 K to 1373 K. The tube furnace cavity can be matched with the α-alumina now tube with an external diameter of 10 mm and length of 500 mm. After passing the flow tube, the reactants and products were detected and identified using a GC-MS system (GC, Agilent Technologies 7890A; MS, Agilent Technologies 5975C) and another GC (Agilent Technologies 7890A) with a flame ionisation detector (FID). The quantification of each species was achieved by combining the external standard and effective carbon number methods [50].

The MB (99%), utilised in this experiment, was purchased from Aladdin Chemical Reagent Co., Ltd. Inert argon gas (99.999%) was used to dilute the fuel and was obtained from Nanjing Special Gases Ltd. The H-type ZSM-5 (HZSM-5) catalyst was purchased from Nankai University Catalyst Co., Ltd. The SiO$_2$/Al$_2$O$_3$ molar ratio of the HZSM-5 was 27 with a specific surface area of 360 m$^2$/g, and 95% of crystallinity.

The total inlet flow rate of MB and argon was fixed at 300 SCCM, where the flow rate of argon was 294 SCCM, and that of liquid MB was 0.03 mL/min, equivalent to 6 SCCM in the gas phase with a mole fraction of 2%. The HZSM-5 catalyst (200 mg) was dispersed and packed in an appropriate amount of silica wool, which was added to the middle of the flow tube with a filling length of 50 mm. The inner diameter of the flow tube was 7 mm.

Before catalytic pyrolysis, HZSM-5 must be activated at a high temperature, so that any absorbed water can be evaporated to improve performance and change the ratio of active sites [51]. The diluted gas was continuously flowed into the pyrolysis tube and when the chamber reached set temperatures at a heating rate of 5 K/min, samples were removed after 10 min. This process eliminated the reaction history of MB during heating. A HP-PLOTQ capillary column was used to separate the pyrolysis products. The oven program of the GC was started at 50 °C, held for 1 min, heated to 180 °C at 15 °C/min, subsequently heated to 220 °C at 10 °C/min, and held at that temperature for 10 min.

All experiments were performed under atmospheric pressure at heated pipeline and vaporiser temperatures of 423 and 413 ± 10 K, respectively. The detailed experimental conditions of each experimental group are listed in Table I. The gas hourly space velocity (GHSV) was estimated using the total inlet flow rate, catalyst filling volume, and experimental temperature range [52].

III. RESULTS AND DISCUSSION

A. Methyl butanoate pyrolysis

As shown in Fig. 2, the main products of MB pyrolysis were methane, ethylene, ethane, propylene, propane, propadiene, propyne, butadiene, and butane. The yields of methane and ethylene were much higher than those of the other products, suggesting that they are the final products of MB pyrolysis. To explore the pyrolysis...
pathways of MB in further detail, a plug flow reactor (PFR) module was used to simulate MB pyrolysis using CHEMKIN-PRO software [53]. The kinetic model used herein was based on previous studies and improved by Zhai et al. [52] for flow tube simulation.

From the simulated reaction pathway analysis (FIG. 3), the primary pathways for MB consumption involve hydrogen abstraction reactions by H atoms, methyl and methoxyl radicals. In contrast, MB consumption via unimolecular dissociation reactions accounted for 2% of total products. Specifically, H-atom abstraction reactions on the α-C and β-C of MB are the main reaction pathways for MB consumption, with branching ratios of 40% and 36%, respectively. Compared to those of methyl and methoxyl, the H-atom abstraction reactions of MB with H atom represent the most important pathways for MB hydrogen abstraction, accounting for 73% of the total consumption. Only 13% and 12% of MB consumption are derived from H-atom abstractions with methyl and methoxyl.

Furthermore, possible formation routes of methane and ethylene products could be proposed from the decomposition of MB radicals. As shown in FIG. 3, the primary MB radicals are CH₃CH₂CHC(=O)OCH₃ (MB2J) and CH₃CH₂CH₂C(=O)OCH₃ (MB3J). Cracking of MB2J produces methyl and methyl acrylate (MA, CH₂=CHCOOCH₃), while methane is easily formed from methyl via H-atom abstraction, and MP3J derived from MA can produce ethylene via β-scission reactions. MB3J is an important source of propylene and propyl, and propyl can be decomposed to methyl and ethylene or transformed into propylene. In addition, primary MB radical consumption yields methyl crotonate (MC), a methyl ester containing a C=C double bond with the same skeletal structure as MB. MC decomposition is comparable to that of MB, starting with H-atom abstraction, eventually leading to molecular skeleton dissociation. Because of its C=C double bond, MC may be a stable source of ethylene.

The mole fractions of the products in FIG. 2(b) are approximately an order of magnitude smaller than those shown in FIG. 2(a), but comparable products were obtained. Propane, propadiene, and propyne could be formed by H-atom abstraction of the propyl radical, while ethane is derived from a similar pathway to ethylene. In summary, MB consumption via pyrolysis was dominated by hydrogen abstraction. The hydrogen abstraction reaction by H-atom attack consumed the majority of MB. The differences in bond dissociation energies of each C–C bond in MB may be the origin of the high yields of methane and ethylene.

B. Pyrolysis of methyl butanoate over HZSM-5

The following section will consider the catalytic pyrolysis of MB on 773 K activated HZSM-5 as an example because of the similar product curves (FIG. 4). Comparing the MB curves in FIG. 2(a) and FIG. 4(a), the initial decomposition temperature of MB using HZSM-5 catalyst was much lower than that of MB pyrolysis. The initial decomposition temperature of MB was <600 K in the presence of HZSM-5, whereas the temperature of MB pyrolysis was approximately 900 K, showing the obvious catalytic effect of HZSM-5 on MB decomposition.

In terms of products, the mole fraction profiles (FIG. 4) show that MB catalytic pyrolysis produced propylene, dimethyl ether, methanol, methane, ethylene, propadiene, isobutylene, cis-2-butene, and trans-2-butene. The high yields of propylene and methanol indicate that the energy barriers of the partial reaction pathways are significantly reduced by the catalyst.
However, the decomposition pattern of MB pyrolysis cannot explain the high yields of propylene and the extremely low yields of methane and ethylene, which is almost the opposite of MB pyrolysis.

Previous studies [54, 55] have demonstrated that dissociation and dehydration are the main decomposition pathways of oxygenated hydrocarbons over HZSM-5. The related decomposition reactions involve the C–O or C=O bonds of oxygenated hydrocarbons. Moreover, a theoretical calculation for another methyl ester, methyl acetate, suggests that dissociating to ketene and methanol is the primary consumption pathway of the ester over HZSM-5 [56]. Therefore, combined with the high yields of methanol and propylene in the MB catalytic pyrolysis, MB was mainly decomposed to methanol and ketene over HZSM-5 by dissociation (FIG. 5). The unsteady ketene was quickly decomposed to propene, the product observed in the experiment. The low yields of methane and ethylene (FIG. 4(b)) were likely derived from the gas-phase dissociation of propyl, but the relatively low temperature decreases the extent of dissociation.

From FIG. 6, the product selectivities of propylene, dimethyl ether and methanol were determined to be 35.1% at 748 K, 7.2% at 673 K, and 18.8% at 848 K, respectively. The selectivity for methanol increases with increasing temperature, indicating that the catalytic selectivity of HZMS-5 increases with increasing temperature. In contrast, the selectivity for propylene and dimethyl ether decreases at relatively high temperatures. The reduction in selectivity of propylene was likely due to the generation of soot precursors, such as aromatics, from propylene and propyl at high temperatures [57–59]. In addition, relatively high temperatures are not conducive for dimethyl ether formation. A special case among the products is that dimethyl ether (FIG. 4(a)) does not appear in the kinetic model of MB pyrolysis, which is likely related to the presence of HZSM-5. The catalytic promotion of methanol dehydration (FIG. 5) to form dimethyl ether has been described in Refs. [60–62] and HZSM-5 has the same behaviour in this MB catalytic pyrolysis.

The other products in FIG. 4(b), isobutylene, cis-2-butene, and trans-2-butene do not appear in the MB pyrolysis. According to previous studies, these compounds are likely converted from the methanol (FIG. 5), which is a function of HZSM-5 that is well-characterised and referred to as a methanol to hydrocarbons (MTH).
reaction [63, 64]. In the MB kinetic model, these butylene isomers can be generated by substitution of propylene with methyl. The relatively high concentration of propylene (FIG. 4(a)) is likely conducive to the formation of these olefins compared to the case of MB pyrolysis (FIG. 2(a)).

Generally, HZSM-5 dramatically altered the decomposition pathways of MB and reduced the initial decomposition temperature. The decomposition of MB was achieved by dissociation over the catalyst instead of hydrogen abstraction. Moreover, the relatively low temperature contributed to the high selectivity for methanol and propylene in the catalytic pyrolysis of MB over HZSM-5.

Although the reduction in the initial decomposition temperature may reflect the catalyst performance, it does not provide for accurate and comprehensive quantification of catalytic performance. The activation energy of reactions is a widely used thermodynamic index that can be used to quantify the difficulty of chemical reactions, and catalyst performance is closely related to activation energy variation. Activation energies are generally obtained using the Arrhenius equation [65]. Because it is difficult to determine the activation energy of elementary reactions from macroscopic experimental data, the obtained results are generally the apparent activation energy of the total reaction. The results are shown in Table II.

From the apparent activation energy of MB listed in Table II, HZSM-5 at both activation temperatures of 373 K and 773 K greatly reduced the apparent activation energy of MB pyrolysis by approximately 30%. The apparent activation energy of propylene formation was also significantly lower than that of MB pyrolysis. The higher activation temperature (773 K) resulted in lower apparent activation energy of MB pyrolysis, while the apparent activation energies of propylene, methanol and dimethyl ether formation show the opposite trend. It has been reported that activation at high temperature can change the relative proportion of Bronsted acid and Lewis acid sites on HZSM-5 [51, 66]. These types of reactive sites interact differently with reagents, so the changes in both reactive sites may cause variation in the apparent activation energies as a function of activation temperature.

### C. Performance of HZSM-5

The decrease in initial decomposition temperature of MB and apparent activation energy both reflected the catalytic performance of HZSM-5. However, the catalyst performance gradually decreased with reaction progress, finally losing its activity. The mole fraction of MB in the presence of HZSM-5 increased abnormally after 800 K, which was likely the result of the rapid catalyst deactivation. However, the mole fraction of MB at this temperature was still lower than that observed during MB pyrolysis, indicating that the catalyst was not completely deactivated. Previous studies have shown that acetic acid, acetone, and butanone can inactivate HZSM-5 at approximately 723 K, causing the proportion of reactants abnormally increase in abundance [55]. However, this condition does not occur during the pyrolysis of butanol and propanol [43]. It
is speculated that inactivation of HZSM-5 is related to the carbonyl in reactants. To further explore MB pyrolysis when HZSM-5 was significantly deactivated, MB catalytic pyrolysis over a wider temperature range was examined. From the comparison shown in FIG. 7, the curves of products such as methane, ethylene, ethane, and propylene during catalytic pyrolysis was quite similar to those of pyrolysis at high temperatures where the catalyst was significantly deactivated. This indicates that the heavily deactivated HZSM-5 may have a negligible further negative effect on MB pyrolysis. Thus, in the presence of deactivated HZSM-5, MB decomposition is still similar to the pyrolysis.

Therefore, variation in HZSM-5 activity with activation temperature prior to deactivation was further investigated. From FIG. 4(a), lower activation temperature led to higher peak mole fractions of the products, with higher peak temperature. It should be noted that the appearance of product peaks is related to both the reaction temperatures and catalyst activity. Herein, the highest catalyst activity occurred during the initial stages of the experiment, but the reaction temperature was low. As the reaction temperature increased, the catalyst activity gradually decreased. Thus, the product peaks were the result of suitable reaction temperatures and sufficiently active catalysts.

IV. CONCLUSION

In this work, it was demonstrated that HZSM-5 could greatly reduce the initial temperature of MB decomposition from approximately 900 K to ≤600 K. Because of the significant reduction in the apparent activation energy of the total reaction by HZSM-5, MB decomposition was achieved by dissociation on the catalyst surface instead of hydrogen abstraction in the gas phase. Therefore, the high-yield products were changed from methane, ethylene, and propene to methanol, propylene, and dimethyl ether. The activation temperature of HZSM-5 also affected catalytic pyrolysis. In terms of the product mole fraction, the activation temperature could shift the temperature where the products peaks were observed. In addition, the activation temperature influenced the apparent activation energies to some extent. Generally, the experiment described above is meaningful for subsequent catalytic MB combustion, and provides guidance for the modification of HZSM-5 for resistance to deactivation. However, more rigorous reaction pathway analysis and a complete kinetic model have not yet been obtained, and these aspects should be addressed in future studies.

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