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Conversion of methylesters to hydrocarbons over an H-ZSM5 zeolite catalyst

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ABSTRACT

The conversion of methyl octanoate on an H-ZSM5 zeolite catalyst has been investigated as a model reaction for the production of hydrocarbon fuels and chemicals from biodiesel. The reactivity of methyl octanoate on H-ZSM5 is higher than that observed with a linear alkane of the same chain length as the ester, n-octane. The enhanced activity may be due to the strong adsorption of the ester group on the zeolite sites. The deoxygenation of methyl octanoate yielded a variety of hydrocarbons (C_1–C_7), with significant amounts of aromatics. Octanoic acid and heavy products, particularly 8-pentadecanone, were formed as primary products from methyl octanoate via acid-catalyzed hydrolysis and condensation, respectively. Both octanoic acid and the condensation products undergo further reaction, producing aromatics. The comparison conducted with n-octane as a feed indicates that aromatics can be formed through a series of reactions, namely cracking, oligomerization, and cyclization. A small amount of ethylbenzene and o-xylene at low conversion of methyl octanoate indicates that direct dehydrocyclization may also take place, but this path was not evident when the feed was n-octane.

1. Introduction

Fatty acid methyl esters (FAMEs) obtained from the transesterification of triglyceride with methanol have received considerable attention as replacements for fossil fuels [1–4]. Advantages of these renewable biodiesels compared to conventional petroleum-derived diesel include their high cetane number, low sulfur content, high flash point, and the cleanness of the exhaust emissions. However, one of the major technical concerns for the biofuels includes the oxidative and thermal instability due to the presence of oxygen [5–8]. The elimination of the oxygen content in biodiesel improves its stability and enhances its utilization potential.

Typically, the deoxygenation of oxygen-containing compounds has been conducted on noble metal catalysts. For instance, Pd/C has been found to be an effective catalyst for the deoxygenation of oxygenates (such as alcohol, carboxylic acid, and ketones) to hydrocarbons [9]. Hydrotreating catalysts, such as CoMo and NiMo supported on Al_2O_3, have also been used for ester deoxygenation under typically high operating pressures [10–12]. To reduce the severity of the operation, several attempts have been made to utilize acid catalysts and transform the oxygen-containing molecules at lower pressures [13,14].

Among the most common acid zeolite catalysts, H-ZSM5 is well known for its remarkable activity for the conversion of alcohols into hydrocarbons [15], which has been demonstrated in many processes, including MTG, MTO, BTG, and BETE [16,17]. The hydrocarbons obtained from the reaction are typically in the gasoline boiling range, with substantial amounts of aromatics. Similarly, several reports have demonstrated the successful application of H-ZSM5 for the transformation of other oxygenates (e.g. acetone) to higher paraffins and olefins [18,19]. The transformation of ketones involves direct decarbonylation to the corresponding olefins in the first step, followed by oligomerization of the olefin. A comparison of the relative reactivities of aldehydes, ketones, and acids on H-ZSM5 has shown that all of them produce olefins and aromatics at high temperatures, but acids are significantly more reactive than aldehydes and ketones [20]. The deoxygenation of these compounds takes place mainly through decarboxylation and dehydration. Recent studies by Corma et al. [21] and Huber and co-workers [22] have shown that H-ZSM5 is an effective catalyst for the conversion of glycerol and sorbitol. In summary, while deoxygenation on H-ZSM5 has been extensively investigated with alcohols, aldehydes, ketones, and biomass-derived sugars, it has been much less studied with biodiesel esters. Hence, in this work, the conversion of methyl octanoate, as a model biodiesel fuel, has been investigated on H-ZSM5. While methyl octanoate is much shorter than the typical esters present in biodiesel, it contains the important chemical functionality

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(CH_3–O–COR) that we are interested in investigating. Having a shorter aliphatic chain makes the analysis and handling much easier than working with esters of longer chains. We have compared the product distribution from this ester with that resulting from an alkane with the same chain length.

2. Experimental

2.1. Catalyst preparation

The H-ZSM5 zeolite catalyst was synthesized following published conventional methods [23] using tetrapropylammoniumbromide (TPABr) as the organic template. The synthesized zeolite was calcined in air at 873 K for 5 h to decompose the organic templates. The resulting Na^+ ions in the synthesized zeolite was exchanged by NH_4^+ ions from a 1 M NH_4NO_3 solution at 353 K for 10 h, using a liquid/solid ratio of 100 ml per gram of zeolite. Then, the zeolite was separated from the solution by filtering and were thoroughly washed. The exchange procedure was repeated three times to complete the Na^+ ion exchange. Subsequently, the catalyst was dried overnight at 383 K and calcined in flowing dry air at 773 K for 5 h to produce the acidic form of the zeolite (H-ZSM5).

2.2. Catalyst characterization

To confirm the zeolite structure and evaluate the crystallinity of the catalyst, XRD was conducted on all samples using a Rigaku X-ray diffractometer with filtered CuK_α line at a scanning rate of 5°/s. Moreover, the zeolite morphology and crystallite size were investigated in a JEOL 5200-2AE SEM scanning electron microscope. Nitrogen adsorption was carried out at 77 K to obtain the BET area of the synthesized H-ZSM5 zeolite catalyst, using a Thermo Finnigan Modeled Sorptomatic 1100 series. Elemental analyses were carried out in a Perkin Elmer Optima 4300 DV inductively coupled plasma optical emission spectrometer (ICP-OES).

The zeolite acidity was quantified by the amine TPD (temperature programmed desorption) technique developed by Gorte and co-workers [24]. The sample (30 mg) was initially pretreated in a flow of He for 1 h at 773 K. Then, the sample was cooled in He to room temperature and 10 μl pulses of propylamine were injected over the sample, until the sample was saturated. The saturation of propylamine adsorption was confirmed by mass spectrometry. After removal of the excess propylamine by flowing He for 3 h, the sample was linearly heated to 973 K at a ramping rate of 10 °C/min. Masses 30, 41, and 17 were monitored to determine the evolution of propylamine, propylene, and ammonia, respectively. The amount of desorbed propylene was calibrated with a 5 ml pulse of 2% propylene in He.

The density and strength of the acidic sites of the catalyst were also characterized by FTIR using pyridine as a probe molecule. Infrared spectroscopic measurements of the adsorbed pyridine (Py-IR) were recorded in a Bruker Equinox 55 spectrometer. The sample (90 mg) was pressed into a 2.5 cm diameter self-supported wafer, placed in a gas-tight cell with CaF_2 windows. Prior to pyridine adsorption, the sample was pretreated in a He flow at 773 K for 2 h. After the pretreatment, the sample was cooled to 423 K, and a blank spectrum was taken. Subsequently, pyridine vapor was introduced into the cell and kept for 2 h in order to saturate the acid sites. The excess pyridine was then purged from the cell by flowing He for 12 h. Four spectra were obtained for each sample at 423 K, both on the saturated sample, and after outgassing at increasing temperatures from 573 to 773 K. The absorption band appearing at 1545 cm^{-1} was assigned to the pyridinium ion formed on the Brønsted acid sites, while the band at 1455 cm^{-1} was assigned to pyridine coordinated to Lewis acid sites. The density of both Brønsted and Lewis acid sites was then quantified by integrating the corresponding absorption bands and using the molar extinction coefficients proposed by Emeis [25].

2.3. Catalytic activity measurements

The catalytic activity tests for the reaction of methyl octanoate were performed in a 1/4 in. quartz tube at 673 and 773 K, at atmospheric pressure. To investigate the selectivities of the products as a function of methyl octanoate (MEO) conversion, the space time (W/F) was varied from 0.2 to 6.4 $g_{cat.}\,h/mol_{MEO}$ in a single-pass continuous flow reactor packed with catalyst powder. Prior to the reaction, the catalysts were treated *in situ* for 1 h in flowing H_2 at the reaction temperature. Methyl octanoate was injected using a syringe pump through a heated vaporization port. The molar ratio of H_2 to feed was kept at 6:1 in all experiments. The products were analyzed by online gas chromatography (Shimadzu GC-17A) using a temperature program to optimize product separation, and a GC/MS (Shimadzu Q5000) for product identification.

3. Results and discussion

3.1. Catalyst characterization

The physical properties of the synthesized H-ZSM5 catalyst derived from XRD, SEM, and nitrogen adsorption are summarized in Table 1. The XRD patterns were fully consistent with those reported in the literature for pure H-ZSM5 [23,26]. The approximate crystallite size determined by SEM was 3 μm. Chemical analysis indicated that the Si/Al ratio was 36, which corresponds to a maximum theoretical Brønsted acidity density of 450 $\mu mol/g_{cat}$. In reasonable agreement, the TPD of propylamine resulted in a density of accessible sites of 382 $\mu mol/g_{cat}$. The distribution of Brønsted and Lewis sites as a function of temperature as measured by FTIR of adsorbed pyridine is presented in Table 2.

3.2. Conversion of methyl octanoate

The conversions of methyl octanoate as a function of time on stream at 673 and 773 K are shown in Fig. 1. It can be seen that at 673 K, a rapid deactivation is evident. At 773 K, the amount of catalyst used is in excess and 100% conversion was observed for a few hours, until the deactivation was apparent. The product distribution varies with the level of conversion and the reaction temperature. First, Table 3 compares the products obtained at the same W/F and same time on stream. It shows that at 773 K, working with excess catalyst, C_2 and C_3 hydrocarbons are the dominant products. In addition, a significant amount of aromatics (i.e. toluene, C_8 aromatics and C_9+ aromatics) were observed. By contrast, at 673 K at the same W/F and same time on stream, the conversion is much lower and octanoic acid and condensation products (namely 8-pentadecanone, tetradecene, and condensation ester) were the major products. Much lower yields of total aromatics were obtained at this temperature.

Second, an analogous comparison of product distribution at the two temperatures was made at similar conversion by varying the

Table 1
Physical properties of the H-ZSM5 catalyst.

	H-ZSM5
Si/Al from chemical analysis	36
BET surface area (m^2/g)	377
Particle size (μm) from SEM	~3
Acidity density ($\mu mol/g_{cat.}$) from TPD of isopropylamine	382