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Kinetic and Spectroscopic Studies of Methyl Ester Promoted Methanol Dehydration to Dimethyl Ether on ZSM-5 Zeolite

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Abstract: Methyl carboxylate esters have been shown to be potent promoters of low-temperature methanol dehydration to dimethyl ether (DME) using various zeolite catalysts. In the present work, catalytic kinetic studies, *in-situ* Fourier-transform infrared spectroscopy (FT-IR) and solid-state nuclear magnetic resonance spectroscopy (NMR) techniques were used to elucidate the promotional mechanism of methyl carboxylate esters on methanol dehydration to DME, using the medium pore zeolite H-ZSM-5 (MFI) as the catalyst. Kinetic studies were performed using the very potent methyl *n*-hexanoate promoter. The DME yield was dependent on both the methanol and methyl *n*-hexanoate partial pressures across the temperature ranges used in this study (110 to 130 °C). This is consistent with the promoted reaction being a bimolecular reaction between methanol and ester species adsorbed at the catalyst active sites, via an S_N2 type reaction, as previously postulated. The *in-situ* FT-IR studies reveal that the Brønsted acid (BA) sites on H-ZSM-5 were very rapidly titrated by ester carbonyl group adsorption and bonded more strongly with esters than with methanol. Upon methanol addition, an even lower DME formation temperature (30 °C) was observed with methyl *n*-hexanoate pretreated H-ZSM-5 samples in the *in-situ* NMR studies, further confirming the strong promotion of this methyl ester on methanol dehydration to DME. The adsorption and reactivity of different methyl esters on H-ZSM-5 indicates that while methyl formate more easily dissociates into a surface methoxy species, [Si(OMe)Al], and carboxylic acid, it is a less potent promoter than alkyl-chain-containing methyl esters in methanol dehydration to DME, which in turn did not show this dissociative behavior in the low-temperature NMR studies. This indicates that methyl alkyl carboxylates do not need to be dissociated to a surface methoxy species to promote the methanol dehydration reaction and that a bimolecular associative mechanism plays an important role in promoting DME formation.

Keywords: methanol dehydration to DME; promotion; methyl *n*-hexanoate; ZSM-5; kinetic; solid-state NMR; FT-IR

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1. Introduction

Zeolites, crystalline hydrated microporous aluminosilicates whose structures enclose channels and/or cavities of molecular dimensions (0.3–1.5 nm diameter), are extremely important heterogeneous catalysts with numerous large-scale applications, including cracking, petrochemistry, fine chemical synthesis, and environmental protection [1–3]. In most industrial applications, the key catalytic functionality is the atomically dispersed acid sites in an ordered porous structure, which provide the so-called confinement effect of the reactants/products and/or the transition states [4]. The confinement of reactive intermediates and transition states within the voids of zeolite is considered a key factor in catalysis by zeolites. Voids provide the “right fit” for certain transition states, reflected in their lower free energies, thus extending the catalytic diversity of zeolites well beyond simple size discrimination [5]. Confinement mediates enthalpy–entropy compromises that determine the Gibbs free energies of transition states. These activation free energies determine the turnover rates, as indicated by transition state theory. In recent times, such solvent-like effects have been widely explored by the kinetic and mechanistic work of Iglesia and coworkers [5–8].

The mechanism of zeolite catalyzed methanol dehydration to dimethyl ether (DME) has been widely studied by many research groups [7,9–13]. These studies have identified two distinctive reaction pathways for the formation of DME. The dissociative reaction pathway involves the formation of a surface methoxy species, [Si(OMe)Al], via adsorption and reaction of methanol on a Brønsted acid site. The surface methoxy species subsequently reacts with a second molecule of methanol to provide DME. In the competing associative reaction pathway, both methanol molecules co-adsorb on the Brønsted acid site to form a dimer species, which then rearranges and reacts to form DME.

Organo-catalysis by confined guest species in zeolite cages has become an emerging research area, because it can heterogenize "organo-catalysis" via the utilization of metal-free, relatively small organic molecules to catalyze a chemical reaction [4]. Indeed, organic residues in the pores of zeolite catalysts play a key role in high-temperature methanol-to-hydrocarbons (MTH) chemistry via the widely studied hydrocarbon pool mechanism. It is commonly agreed that olefins are formed by the reaction of methanol with these organo-species (such as heptamethylbenzenium cation and pentamethylcyclopentenyl cation) and their following transformations [14–17].

In our previous fundamental studies aimed at understanding the impact of impurities on methanol dehydration to DME, it was discovered that a wide range of organic carbonyl compounds and their derivatives (carboxylate esters, carboxylic acids, ketones, ketals, aldehydes and acetals) promote DME formation on various acidic zeolites (H-SSZ-13, H-ZSM-5, H-beta and H-mordenite) [18]. By taking advantage of the well-known confinement effect, in combination with further functionalization, the potency of the promoter can be markedly enhanced, resulting in significant increases in the DME yield at promoter concentrations as low as 10 ppm relative to methanol. The promoters allow for an improved catalyst performance to be achieved with readily and widely available commercial zeolites, such as ZSM-5, without the need to resort to elaborate, expensive and time-consuming synthesis and scaling up of bespoke materials.

In the methyl carboxylate ester promoted methanol dehydration on H-ZSM-5 catalyst, the DME space–time yield increases systematically with the methyl carboxylate ester chain length, from formate to *n*-hexanoate [18]. Based on the initial experimental and molecular modeling studies, it was proposed that the methyl carboxylate ester creates an additional catalytic cycle in which the more reactive ester promoter reacts with methanol to form DME. In the second part of this cycle the carboxylic acid regenerates the promoter species via a fast esterification reaction with methanol. In the present work, reaction kinetics and *in-situ* spectroscopic studies (FT-IR and solid-state NMR) were carried out to study the methyl *n*-hexanoate promoted methanol dehydration to DME over H-ZSM-5 zeolite to further elucidate the promotional mechanism of the carboxylate esters in methanol dehydration to DME on zeolites.

2. Materials and Methods

2.1. Materials

The zeolite catalysts ZSM-5 SAR23, with a silica-to-alumina ratio (SAR) of 23 (Product code: CBV2314), and ZSM-5 SAR80, with a silica-to-alumina ratio of 80 (Product code: CBV8014), were obtained from Zeolyst International (Conshohocken, PA, USA) in the ammonium form. The catalysts were converted into their H-form by calcination under air at 500 °C in a furnace, and the corresponding samples are denoted as H-ZSM-5 SAR23 and H-ZSM-5 SAR80. Methanol (CHROMASOLV™, HPLC), methyl formate (anhydrous, 99%), methyl propionate (99%, AR), methyl butyrate (99%, AR) and methyl hexanoate (99%, AR) were purchased from Sigma-Aldrich (Merck, Darmstadt, Germany). ^{13}C-enriched methanol ($^{13}CH_3OH$) was purchased from Cambridge Isotope Laboratories Inc. (Tewksbury, MA, USA).

2.2. Material Characterization

Powder X-ray diffraction (XRD) patterns were acquired on an EMPyrean-100 XRD diffractometer from Malvern Panalytical Limited (Worcestershire, UK), with a CuKα radiation source. The diffraction data in a 2θ range of 5°~50° were collected. A morphological analysis was conducted using a FEI (Thermo Fisher Scientific Inc, Waltham, MA, USA) Nova Nanosem450 field emission scanning electron microscope (SEM). An ammonia temperature programmed desorption (NH_3-TPD) analysis was carried out using a fully automated Altamira AMI-200 Chemisorption Analyser. Approximately 50 mg of sample was accurately weighed into a quartz U-shaped reactor tube. The reactor tube outlet was plugged using quartz wool that had been pretreated in an oven at 120 °C. The reactor tube was then placed in the AMI-200 unit and pretreated *in-situ* under a flow of dry argon, heating from room temperature to 400 °C at 10 °C/min and dwelling for 60 min to dry the sample. The sample was cooled to 100 °C, and NH_3 loading was carried out by flowing a 1% NH_3/Ar mix (30 mL/min) for 60 min (or until saturation was reached). While maintaining the bed temperature at 100 °C, any physiosorbed and other weakly adsorbed materials were then purged from the surface by treating with water vapor for 60 min. The sample was further treated with a flow of dry argon at 100 °C for 60 min in order to remove any residual water from the sample bed. Finally, a TPD analysis was carried out by heating the sample from 100 to 800 °C at a rate of 5 °C/min under flowing argon (30 mL/min). The NH_3 desorption was continually monitored throughout using a Mettler Toledo T50 acid–base autotitrator. This mode of detection utilizes a Kjeldahl-style pH stat method, whereby ammonia that desorbs from the sample is delivered to a dilute boric acid receiver solution. The pH of this solution is constantly maintained at 5 by adding a 0.02 M HCl titrant. The volume of HCl required to sustain a constant pH can be used to calculate the amount of NH_3 that has desorbed from the sample. The results are expressed as µmoles of H^+ per gram of catalyst based on the NH_3 desorbed per loaded mass of sample.

2.3. Kinetic Tests

The reaction kinetic studies of methanol dehydration to DME promoted by methyl *n*-hexanoate were carried out using a 16-channel parallel fixed-bed reactor Flowrence™ system from Avantium N.V., using stainless-steel reactors with a 2 mm internal diameter and length of 300 mm. The Flowrence™ unit was equipped with four independently controlled temperature blocks, one per each of the four reactors, allowing a range of temperatures and catalysts, plus a blank control reactor, to be simultaneously tested in a single experiment. The liquid feed was introduced by an HPLC pump into a heated zone (220 °C) along with inert gas feeds before feeding to the reactors. In a typical experiment, fifteen of the reactors were packed with 25 mg of catalyst, which had a particle size fraction of 100 to 200 µm in diameter. The sixteenth reactor was packed with carborundum only. After a gas distribution test, each reactor was heated under a flow of inert gas (nitrogen mixed with helium at a volumetric ratio of 10:1 at 2.68 normal liters per hour per reactor), to a designed reaction temperature (110 to 150 °C) at a total pressure of 1100 kPa. After

1 h at the reaction temperature, a gaseous feed comprising 10 mol% methanol and inert gas (nitrogen mixed with helium as an internal standard, with a volumetric ratio of 10:1) was then introduced into each reactor for a period of 24 h. The total volumetric feed rate of the gases and vaporized liquid feed was 2.98 normal liters per hour per reactor. After 24 h, methyl *n*-hexanoate was added to the methanol to achieve a gaseous feed comprising methanol and methyl *n*-hexanoate with designed partial pressures, the nitrogen flow being reduced to keep the total volumetric feed rate of the gases and vaporized liquid feed at 2.98 normal liters per hour per reactor. Dew point calculations were performed to ensure that the methyl *n*-hexanoate promoter was tested at partial pressures such that it remained in the vapor phase at the inlet to the reactors. The effluent stream from each reactor was diluted with inert gas (nitrogen) and periodically analyzed by online gas chromatography to determine the space time yields (STYs) in gram per kilograms of catalyst per hour (g kg^{-1} h^{-1}) of DME product. The methanol conversion in all of the experiments reported here was far away (below 35% and in most cases much lower than this) from equilibrium conversion to DME (95% at 110 °C). Under these low conversion conditions, in the presence of excess methanol, methyl esters pass over the zeolite catalyst largely unconverted and carboxylic acids are rapidly esterified [18].

Due to the potency of the promoters tested on the Flowrence™ unit used in this work, the standard testing protocol used fresh and clean methanol at the start of each experiment to ensure that baseline conditions had been reestablished before subsequently testing the methyl *n*-hexanoate promoter in the unit. A DME STY measurement was routinely taken 18 to 24 h after first introducing methanol to the unit. In addition, the process lines were flushed with clean methanol at the end of each experiment to remove any traces of promoter from the testing equipment. Using this procedure, the Flowrence™ unit gives excellent reproducibility; a control sample of H-ZSM-5 SAR80 tested 82 times at 150 °C and a methanol WHSV of 17.1 h^{-1} resulted in a DME STY of 388 ± 20 g kg^{-1} h^{-1}. Once the baseline conditions had been established, the reaction conditions were then varied by changing the partial pressure of the reactants, with the DME STY measurements taken once steady-state conditions were observed.

2.4. FT-IR Spectroscopic Analysis

Fourier-transform infra-red (FT-IR) spectra were collected using a high-temperature reaction cell from Harrick Scientific (Pleasantville, NY, USA). The reaction cell was equipped with ZnSe windows, and it was operated at ambient pressure. The FT-IR spectra were collected with a Thermo Fisher Nicolet™ 6700 spectrometer (Thermo Fisher Scientific Inc, Waltham, MA, USA) equipped with an MCT detector and KBr beam-splitter and were measured in the transmission mode. In a typical experiment, approximately 10 mg of zeolite powder was made into a disk by pressing, which was then placed in a sample holder in the reaction cell. The zeolite sample was degassed of air and dried under flowing nitrogen at 450 °C for 2 h, with the sample having been heated to 450 °C at a ramp rate of 5 °C/min. The zeolite sample was then cooled to 110 °C. The reactant under study (i.e., methanol or methyl *n*-hexanoate) was then introduced into the reaction cell by sparging nitrogen through the liquid reactant placed in a saturator operated at room temperature. The partial pressure of each reactant was set by its saturated vapor pressure at ambient temperature, e.g., ~17 kPa for methanol at 25 °C. The flowrate of the nitrogen was 50 mL per minute in all cases. After an appropriate reaction time, the reaction cell was then purged with nitrogen at 110 °C for 2 h to remove any weakly held physiosorbed surface species from the zeolite. An additional reactant (i.e., methanol) was optionally introduced into the reaction cell, with the sample still at 110 °C following the nitrogen purge, by changing the liquid in the saturator. The FT-IR spectra of the zeolite sample were recorded, with wavenumbers ranging from 1200 to 4000 cm^{-1}. The spectra were collected at a frequency of one per minute, using 32 scans per spectrum. The time-resolved plots of the FT-IR spectra were created based on desirable time intervals to show the major changes that occurred.

2.5. NMR Spectroscopic Analysis

For the *in-situ* NMR study of methanol dehydration to DME without methyl *n*-hexanoate, 0.2 g of the H-ZSM-5 sample was dehydrated under high vacuum (10^{-4} Pa) at 420 °C for 12 h. Then, it was exposed to 1 kPa methanol vapor and equilibrated at 70 °C for 1 h. The excess methanol was removed by evacuating the sample for 30 min. The sample was transferred into NMR rotors in a glove-box for the NMR experiment. The ^{13}C cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were taken while the temperature was increased to 30, 40, 60, 70 and 120 °C.

For the *in-situ* NMR study of methanol dehydration to DME over methyl *n*-hexanoate-doped H-ZSM-5, methyl *n*-hexanoate adsorption was conducted by exposing 0.2 g of dehydrated H-ZSM-5 to 0.2 kPa of methyl *n*-hexanoate for 30 min. Subsequently, the excess ester was desorbed under vacuum for 30 min. The methyl *n*-hexanoate adsorbed sample was further exposed to 2 kPa of ^{13}C-methanol and equilibrated. Finally, the physically adsorbed methanol was removed by evacuation of the sample under vacuum for 4 h. The sample was then transferred into NMR rotors in a glove-box for the NMR experiment. The ^{13}C CP/MAS NMR spectra were taken while the temperature was increased to 30, 40, 60, 70 and 100 °C.

For the methyl formate and methyl *n*-propionate adsorption, 0.2 g of dehydrated zeolite was exposed to 5 kPa of the respective ester and equilibrated at 25 °C for 30 min. Subsequently, the excess ester was desorbed under vacuum for 30 min. For methyl *n*-hexanoate and methyl *n*-butyrate adsorption, 0.2 g of dehydrated zeolite was exposed to 0.2 and 2 kPa of the corresponding esters and equilibrated at this pressure for 2 h at 70 °C. All samples were transferred into NMR rotors in a glove-box for the NMR experiments.

All NMR experiments were carried out using a Bruker AVANCE III 400 MHz NMR spectrometer (Bruker Corporation, Billerica, MA, USA) using a 4 mm double resonance probe with a sample spinning rate of 4–6 kHz.

3. Results and Discussion

3.1. Characterization

Both ZSM-5 SAR23 and ZSM-5 SAR80 have a similar BET surface area of 425 m^2/g [19]. Figure 1 shows the XRD patterns of the H-ZSM-5 SAR23 and H-ZSM-5 SAR80 samples. The zeolites have the typical patterns (denoted by an asterisk in Figure 1) of the ZSM-5's structure. The morphologies of H-ZSM-5 SAR23 and H-ZSM-5 SAR80 were analyzed by SEM. The obtained images show that both samples have a morphology of aggregates of small crystals, as illustrated in Figure 2. The acidity of the two samples was determined by ammonia temperature programmed desorption (NH_3 -TPD). The acidity of the H-ZSM-5 SAR23 sample was 912 µmoles H^+ g^{-1}. The H-ZSM-5 SAR80 sample had an acidity of 346 µmoles H^+ g^{-1}.

3.2. Reaction Kinetic of Promoted Methanol Dehydration to DME

The influence of the methanol's partial pressure and methyl *n*-hexanoate's partial pressure on the DME yield in the methanol dehydration to DME was studied on an H-ZSM-5 SAR80 catalyst at different reaction temperatures (110, 120 and 130 °C). Figure 3 shows the DME STY of the H-ZSM-5 SAR80 catalyst at three different reaction temperatures, with methyl *n*-hexanoate partial pressures between 0 and 0.165 bar; the methanol partial pressure was maintained at 1.1 bar. The DME yield shows a similar trend with an increasing methyl *n*-hexanoate partial pressure at the three reaction temperatures studied. The DME STY increased with an increasing methyl n-hexanoate partial pressure and approached a maximum when the methyl *n*-hexanoate partial pressure was at 0.055 bar. Figure 4 shows the DME yield versus methanol partial pressure, with a constant partial pressure of the methyl *n*-hexanoate (0.11 bar) at three different reaction temperatures (110, 120 and 130 °C). The DME STY increased with an increasing methanol partial pressure, with saturation kinetics being observed.

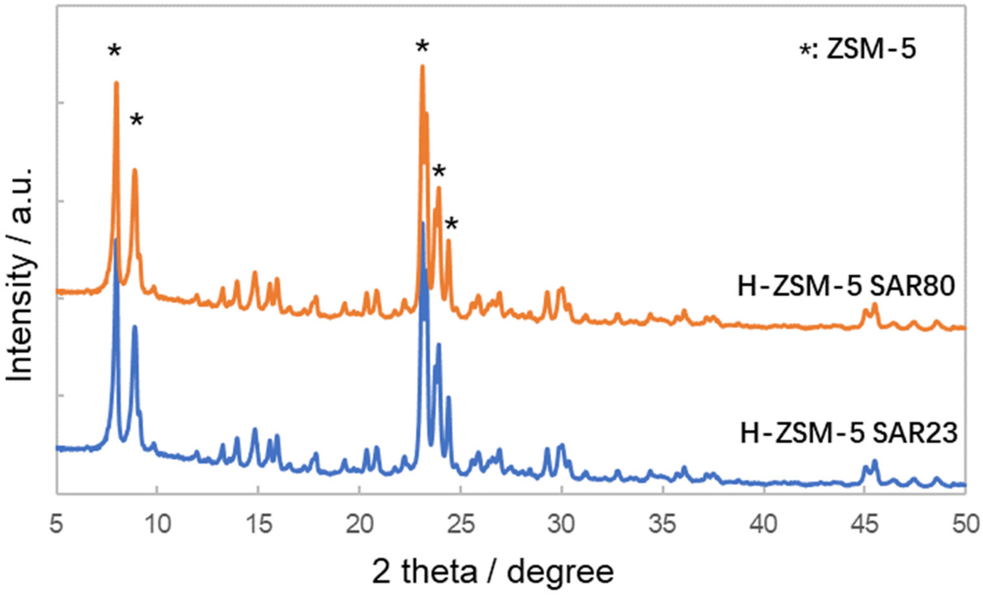

Figure 1. XRD patterns of H-ZSM-5 SAR23 and H-ZSM-5 SAR80.

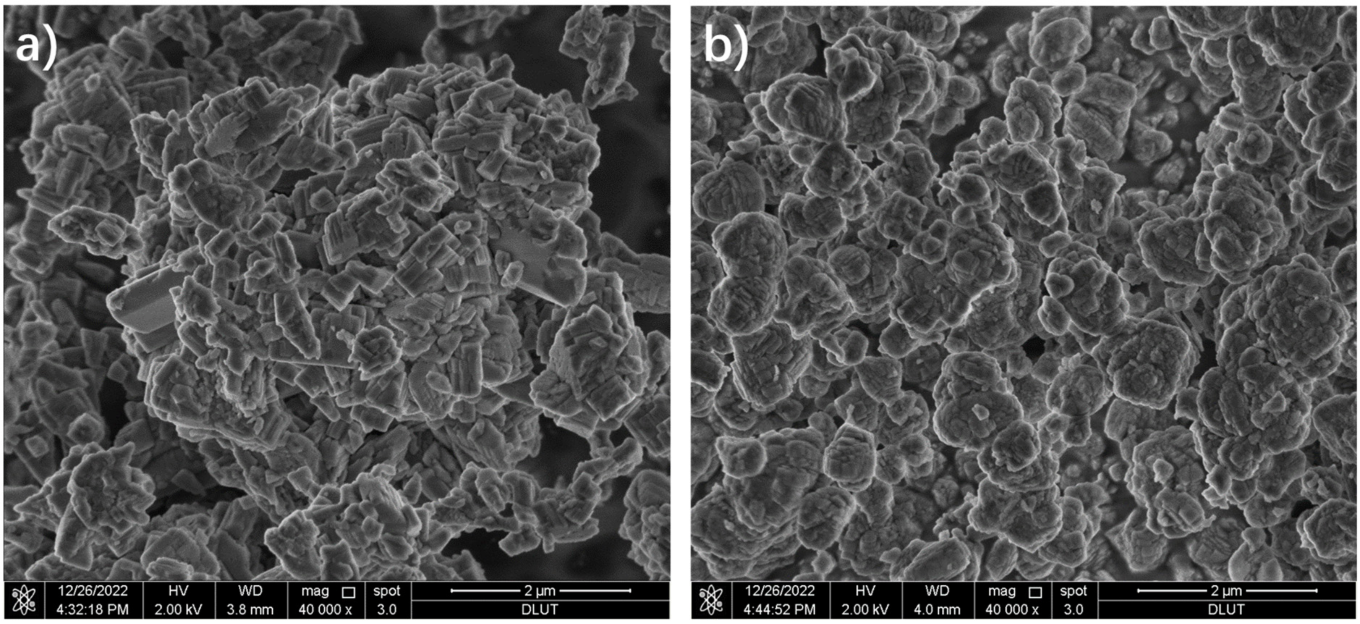

Figure 2. SEM images: (**a**) H-ZSM-5 SAR23; (**b**) H-ZSM-5 SAR80.

The apparent activation energy was determined for H-ZSM-5 SAR80 with 1.10 bar methanol plus 0.11 bar methyl *n*-hexanoate. The turn over frequency (TOF) was calculated according to the DME STY, and the acidity of H-ZSM-5 SAR80 was as shown in Equation (1).

$$\mathrm{TOF} = \frac{\text{DME space time yield}}{\text{acid density}} \tag{1}$$

The data were collected in a temperature range such that the methanol conversion was kept below 10%. An Arrhenius plot of the data collected is shown in Figure 5. The apparent activation energy for the methanol-only reaction was determined to be 109 kJ mol^{-1}, while in the presence of the 0.11 bar methyl *n*-hexanoate it was found to be lowered to 83 kJ mol^{-1}. This is indicative of a change in the reaction pathway and mechanism.

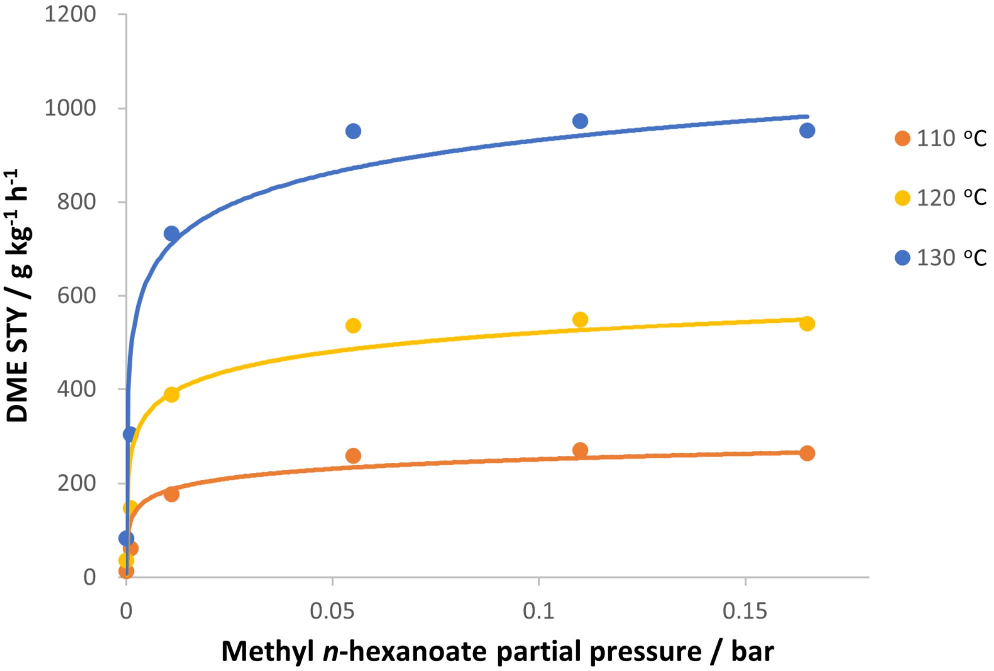

Figure 3. DME STY of the H-ZSM-5 SAR80 catalyst versus the partial pressure of methyl *n*-hexanoate cofed with 1.1 bar methanol at different reaction temperatures: 110, 120 and 130 °C. The curves are guides for the eye only.

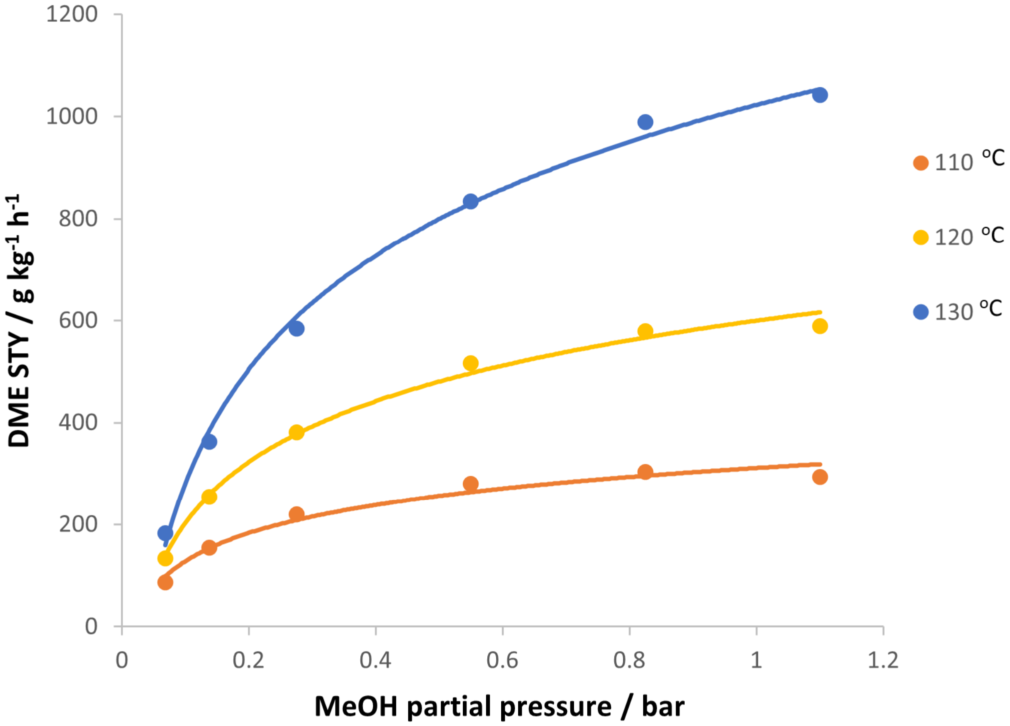

Figure 4. DME STY of the H-ZSM-5 SAR80 catalyst versus the methanol partial pressure cofed with 0.11 bar methyl *n*-hexanoate at different reaction temperatures: 110, 120 and 130 °C. The curves are guides for the eye only.

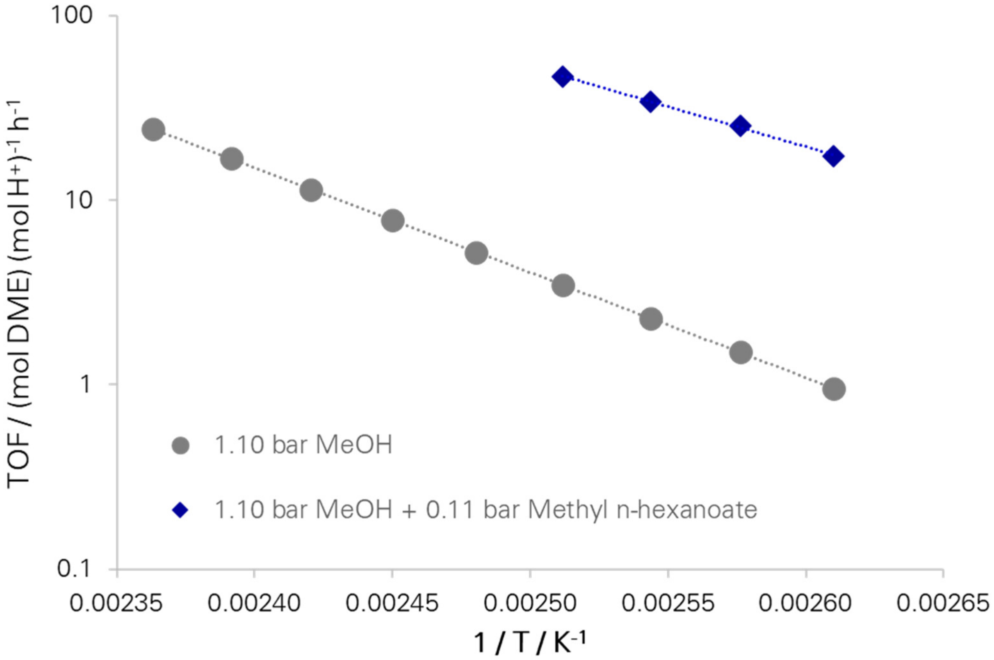

Figure 5. Arrhenius plot for H-ZSM-5 SAR80 with methanol-only feed and methanol plus methyl *n*-hexanoate feed. Conditions: methanol—WHSV 17.1 h^{-1}; methanol partial pressure—1.10 bar; ester partial pressure—0.11 bar; temperature range—110 to 150 °C for the methanol-only feed and 110 to 125 °C for the ester-containing feed.

Overall, the kinetic study results reveal that the DME yield was dependent on both methanol and methyl *n*-hexanoate partial pressures across the partial pressure and temperature ranges tested. This indicates that the promoted reaction may be a bimolecular reaction between methanol and ester species adsorbed at the catalyst's active sites.

3.3. FT-IR Study

3.3.1. Methyl *n*-Hexanoate Adsorption

In our previous molecular modeling work, the adsorption energy of the methyl carboxylate esters was determined, with the carbonyl group interacting with a representative Brønsted acid site at the intersection of the straight and sinusoidal channel of H-ZSM-5, with the alkyl chain on the carboxylate carbon pointing along the straight channel and the carboxylate group pointing into the sinusoidal channel [18]. The results of the molecular modeling work show that the methyl carboxylate esters have a higher adsorption energy than methanol. In the present work, the adsorption of methyl carboxylate esters on H-ZSM-5 zeolites was investigated in detail via *in-situ* FT-IR using methyl *n*-hexanoate as a probe molecule. The FT-IR difference spectra during the doping of the H-ZSM-5 SAR80 zeolite with methyl *n*-hexanoate at 110 °C over the initial 5 min is shown in Figure 6.

The decrease in the intensities of the observed frequencies (i.e., negative peaks) at 3740 cm^{-1}, ascribed to terminal silanol groups (Si-OH-Si), and 3609 cm^{-1}, ascribed to bridging O-H stretching in the Si-OH-Al groups (i.e., Brønsted acid sites of zeolite) [20], indicates the interaction of the methyl *n*-hexanoate molecules with the hydroxyl groups of the zeolite that act as proton donors. The negative peak at 3609 cm^{-1} reached a maximum when the doping time was 2 min, which indicates a fast titration of the Brønsted acid sites by methyl *n*-hexanoate due to the strong interaction. Furthermore, the broad band observed in the 2600 to 2200 cm^{-1} region (centered at 2411 cm^{-1}), which appeared during the exposure of the zeolite to methyl *n*-hexanoate, is ascribed to the O-H stretching modes associated with bridging O-H groups (from the Brønsted acid sites in the zeolite) hydrogen bonded to methyl *n*-hexanoate [21,22]. The C-H stretching vibrations of the $-CH_3$ and $-CH_2-$ groups in methyl *n*-hexanoate were observed in the region of 3200–2750 cm^{-1} [23]. The frequencies observed at 2010 and 1893 cm^{-1} are attributed to the reduction in the intensity of the overtone bands of the zeolite lattice vibrations due to the adsorption of methyl *n*-hexanoate on the zeolite [24]. The vibrational peak at 1478 cm^{-1} was found in the IR spectrum of all molecules containing methylene (-CH_2-) groups and can be thus attributed to the -CH_2- deformation vibrations of the methyl *n*-hexanoate hexyl group, while the peak centered at 1449 cm^{-1} was assigned to the asymmetric C-H bending vibrations of the CH_3 of the hexyl group [23]. The very weak peak observed at a frequency of 1412 cm^{-1} might be ascribed to the symmetric C-H bending vibrations of the methyl group of methyl *n*-hexanoate.

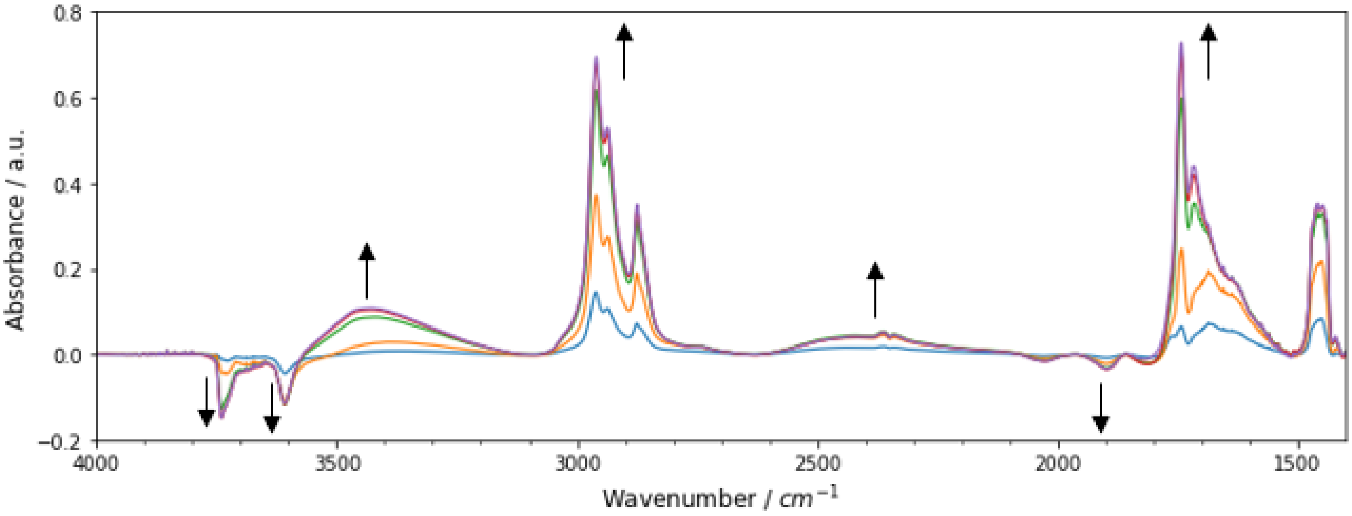

Figure 6. FT-IR difference spectra of methyl *n*-hexanoate adsorption on H-ZSM-5 SAR80 zeolite at 110 °C collected once per minute. The arrows indicate change in the spectrum over time.

The bands found at 1750, 1680 and 1630 cm^{-1} are attributed to C=O stretching vibrations in methyl *n*-hexanoate [25]. In order to elucidate the influence of Brønsted acid sites on the interaction of methyl *n*-hexanoate with the HZSM-5 zeolite and the origin of these three carbonyl stretching vibrations, the H-ZSM-5 SAR80 was subject to a two hour purge with nitrogen after being doped with methyl *n*-hexanoate for 1 h. The FT-IR spectra obtained before and after the nitrogen purge are compared in Figure 7. The intensities of the peaks at 1750 and 1680 cm^{-1} decreased obviously, while the peak intensity at 1630 cm^{-1} did not change after the nitrogen purge. This indicates that the absorbances at 1750 and 1680 cm^{-1} were from C=O weakly bonded to the zeolite. Omid Mowla and coworkers studied the adsorption of ethyl acetate on ZSM-5 zeolite, and their results show that the absorbance at 1750 cm^{-1} can be attributed to weakly adsorbed C=O on the silanol groups of zeolite [26]. The band at 1680 cm^{-1} is most likely due to the adsorption of methyl *n*-hexanoate on Lewis sites resulting from defect sites such as extra-framework aluminum. The main carbonyl band at 1630 cm^{-1} was due to the C=O hydrogen bonded to Brønsted acid sites. The broad peak from 3200 to 3550 cm^{-1} in Figure 7 also decreases obviously after the nitrogen purge. It is suspected that this broad band (appearing in both Figures 6 and 7) may be from the shift in the vibrations of the silanol groups due to the fact of a weak interaction with the ester. In Figure 7, the intensities of the C-H vibration peaks in the region of 3200–2750 cm^{-1} decrease upon the nitrogen purge, which is a sign of the removal of physiosorbed surface methyl *n*-hexanoate species. Overall, the Brønsted acid sites on H-ZSM-5 can be titrated rapidly by the adsorption of methyl *n*-hexanoate.

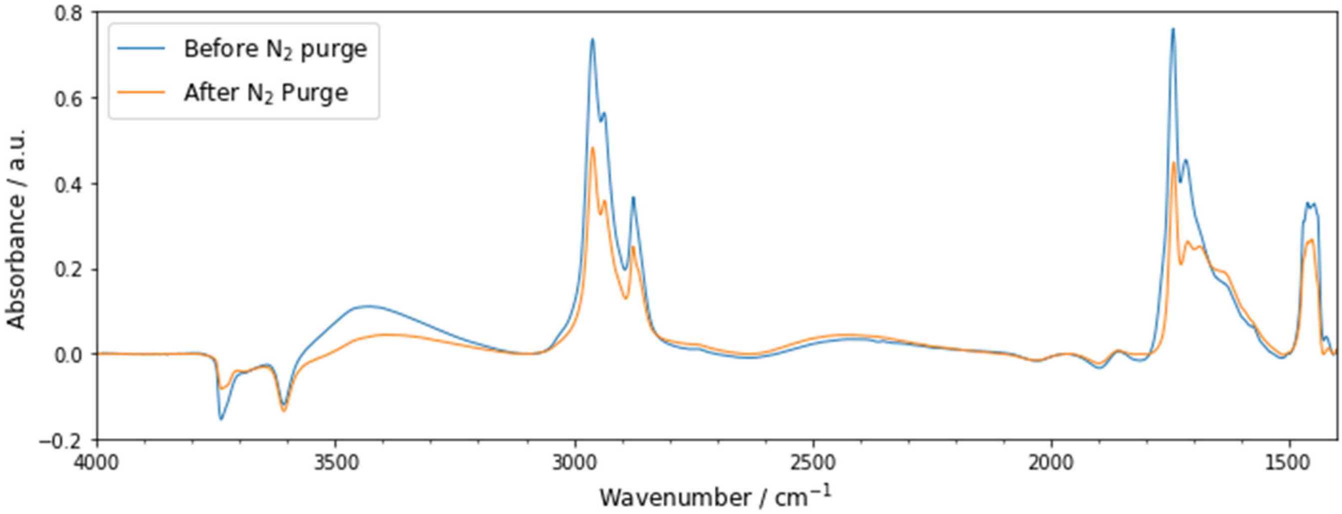

Figure 7. FT-IR difference spectra of H-ZSM-5 SAR80 zeolite doped with methyl *n*-hexanoate before and after the nitrogen purge.

3.3.2. *In-Situ* FT-IR of Methanol Dehydration to DME over Methyl *n*-Hexanoate-Doped Zeolite

Methanol dehydration to DME over methyl *n*-hexanoate-doped H-ZSM-5 SAR80 was investigated by *in-situ* FT-IR, as shown in Figure 8. Over fresh catalyst (blue spectrum in Figure 8) prior to exposure to methanol or methyl *n*-hexanoate, a clear band at 3609 cm^{-1} ascribed to Brønsted acid sites can be observed. After the methyl *n*-hexanoate doping and N_2 purge (purple spectrum in Figure 8), the band at 3609 cm^{-1} disappears. New bands in the region of 3200–2630 cm^{-1}, assigned to the C-H stretching vibrations of methyl *n*-hexanoate, and bands at 1750, 1680 and 1630 cm^{-1}, attributed to C=O stretching vibrations, appear. These peaks indicate the adsorption of methyl *n*-hexanoate on H-ZSM-5 SAR80. Methanol was introduced to methyl *n*-hexanoate-doped H-ZSM-5 SAR80 for 1 h to carry out the methyl *n*-hexanoate promoted methanol dehydration to DME (green spectrum). The surface was dominated with methanol with reduced intensities of IR bands in the range of 1500–2200 cm^{-1}. After purging with nitrogen for 2 h, a new FT-IR spectrum was collected, as shown in black in Figure 8, which removed methanol vapor and physiosorbed methanol. The bands of the aliphatic groups of methyl *n*-hexanoate and Brønsted acid sites bonded C=O in the 1600–1700 cm^{-1} range are still observable. In comparison, a spectrum was collected (shown in blue) for methanol dehydration on ZSM-5 SAR80 without methyl *n*-hexanoate doping, and upon nitrogen purge a pair of bands from surface methoxy species was observed at 2958 and 2856 cm^{-1} [27]. It can thus be seen that some methyl *n*-hexanoate was still adsorbed on the catalyst even though the sample had been flushed with methanol vapor at 110 °C for 1 h. This suggests that the methyl *n*-hexanoate binds with the Brønsted acid sites of the zeolite more strongly than methanol. This result is consistent with our previously reported calculations of the relative adsorption energies of methanol and methyl *n*-hexanoate on a representative Brønsted acid site in H-ZSM-5 (-86 kJ mol^{-1} versus -286 kJ mol^{-1}) [18].

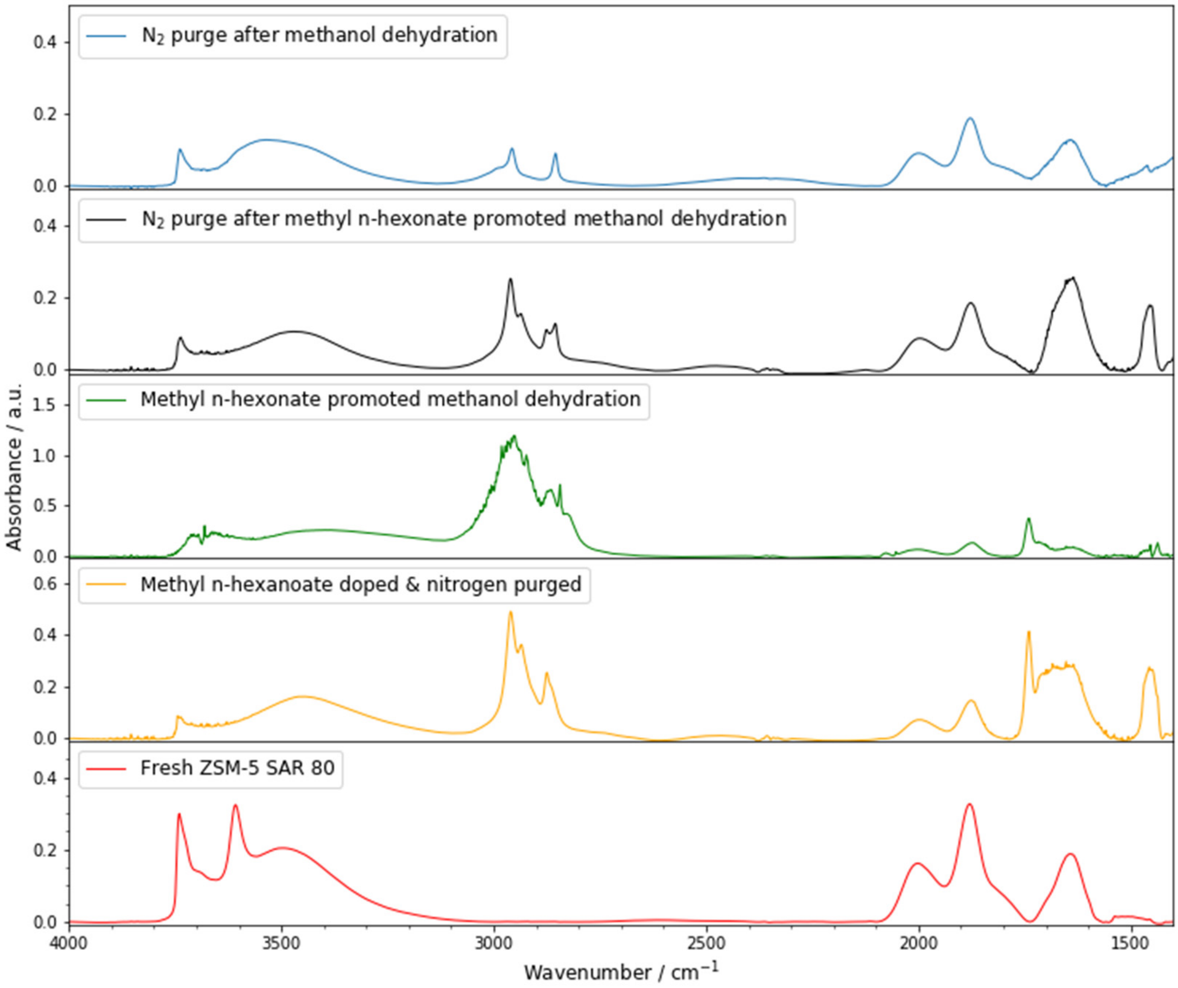

Figure 8. *In-situ* FT-IR of methanol dehydration to DME over methyl *n*-hexanoate-doped H-ZSM-5 SAR80 at 110 °C.

3.4. NMR Study

3.4.1. *In-Situ* Solid-State NMR

In order to obtain a stronger NMR signal, the H-ZSM-5 SAR23 sample, which has a higher acid density, was chosen as the zeolite catalyst for the NMR studies. In previously reported catalytic tests [18], we showed that methyl esters significantly promote DME formation from H-ZSM-5, with an SAR of 23, as well as with an SAR of 80. Firstly, methanol dehydration to dimethyl ether without an ester additive over H-ZSM-5 SAR23 was studied by the *in-situ* NMR technique. After $^{13}CH_3OH$ adsorption and evacuation, ^{13}C CP/MAS NMR spectra were acquired at elevated temperatures from 30 to 120 °C (as shown in Figure 9a). In addition to the signal of methanol at approximately 51 ppm, a small peak that can be assigned to absorbed surface methoxy species was also observed at 57 ppm. A new signal at 59 ppm, which can be assigned to DME, did not appear until the temperature was increased to 120 °C. As shown by the NMR spectra labeled “70 °C—60 min” in Figure 9a, no DME formation could be observed, even when the sample was kept at 70 °C for 60 min. This indicates that without ester addition, methanol only started to dehydrate to form DME at 120 °C over H-ZSM-5 SAR23.

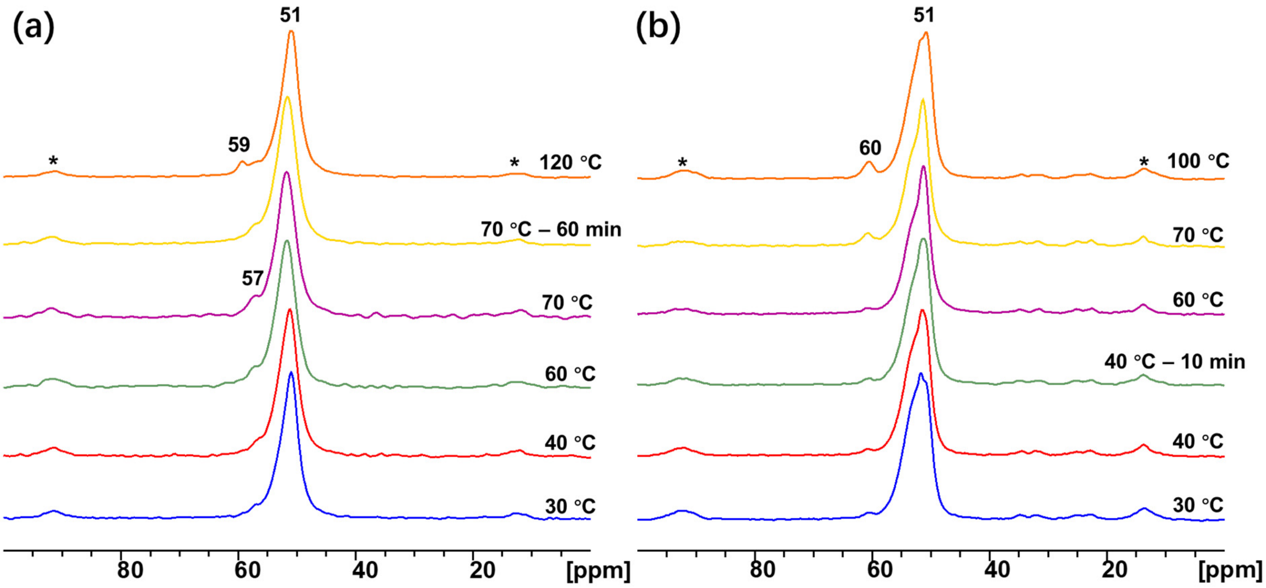

Figure 9. *In-situ* ^{13}C CP/MAS NMR study of methanol dehydration (**a**) without adding methyl *n*-hexanoate on H-ZSM-5 SAR23 at elevated temperatures; (**b**) with methyl *n*-hexanoate addition on H-ZSM-5 SAR23 at elevated temperatures. * Denotes spinning sidebands.

An *in-situ* NMR study of methanol dehydration to DME over methyl *n*-hexanoate pre-doped H-ZSM-5 SAR23 was carried out in a similar way, without the ester additive, except for the sample that was pretreated by a saturated vapor of ester before introducing the adsorption of $^{13}CH_3OH$. The collected ^{13}C CP/MAS NMR spectra can be seen in Figure 9b. The signals of the methyl groups of methyl hexanoate were observed at approximately 51 ppm. The weak peaks in the range from 20 to 40 ppm were from the aliphatic groups from methyl *n*-hexanoate. The DME signal at 60 ppm surprisingly appeared even at the starting temperature of 30 °C. The signal intensity increased as the temperature increased to 100 °C. The significantly lower temperature for DME formation clearly verifies that methyl *n*-hexanoate can promote methanol dehydration to DME on zeolite.

3.4.2. Adsorption of Methyl Esters with Different Alkyl Chain Lengths

The adsorption of the different methyl esters over H-ZSM-5 SAR23 was studied by solid-state NMR. The ^{13}C CP/MAS NMR spectra of methyl formate, methyl *n*-propionate, methyl *n*-butyrate and methyl *n*-hexanoate adsorbed on H-ZSM-5 SAR23 are shown in Figure 10. Generally, the signals near 52–54 ppm can be assigned to the methoxy groups in esters. Signals above 160 ppm can be assigned to carbonyl groups in esters and acids. Signals in the range from 0 to 40 ppm are assigned to the alkane chains on the carboxylate carbon in the esters. It is worth noting that when methyl formate is adsorbed on H-ZSM-5 SAR23, it is partially dissociated into formic acid and a surface methoxy species, [Si(OMe)Al], with signals at 173 and 57 ppm, respectively, whereas no dissociative adsorption of other esters is observed, even when the adsorptions of methyl *n*-butyrate and methyl *n*-hexanoate on H-ZSM-5 SAR23 were carried out at 70 °C. Prior to the work reported here, a systematic full catalytic study was conducted aimed at exploiting the confinement effect by modifying the size of the methyl carboxylate ester. Varying the length of an alkyl chain on the carboxylate carbon was shown to increase the promoter potency by more firmly anchoring the promoter in the zeolite micropore channels. The DME STY increased systematically with the methyl carboxylate ester chain length, all the way from formate to *n*-hexanoate [18]. The present NMR work indicates that methyl formate can be more easily dissociated to form surface methoxy species than the longer alkyl chain methyl esters. Therefore, it can be concluded that the surface methoxy species formed from the dissociation of methyl esters via the dissociative route may not be important reaction intermediates for methyl ester promoted methanol dehydration to DME over zeolite catalyst. A bimolecular associative mechanism may play a more important role, as shown by the mechanism scheme in Figure 11. However, we do not rule out that a dissociative mechanism might also operate in some instances and be may difficult to detect under industrially relevant and forcing catalytic conditions, where high methanol and promoter coverages are present, obscuring more highly reactive intermediates.

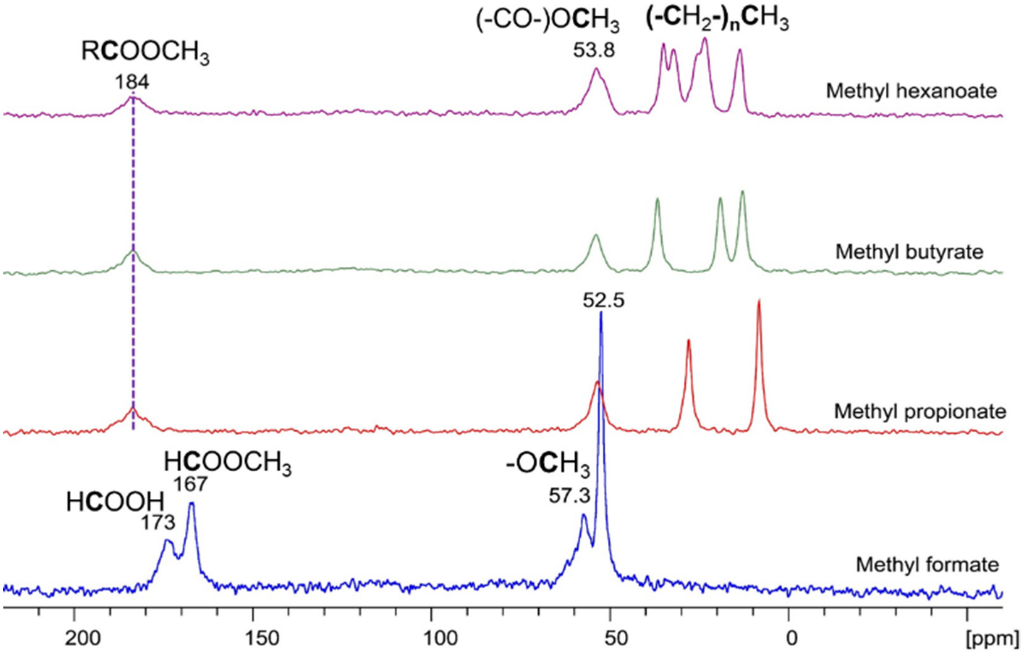

Figure 10. ^{13}C CP/MAS NMR spectra of different methyl esters adsorbed on H-ZSM-5 SAR23.

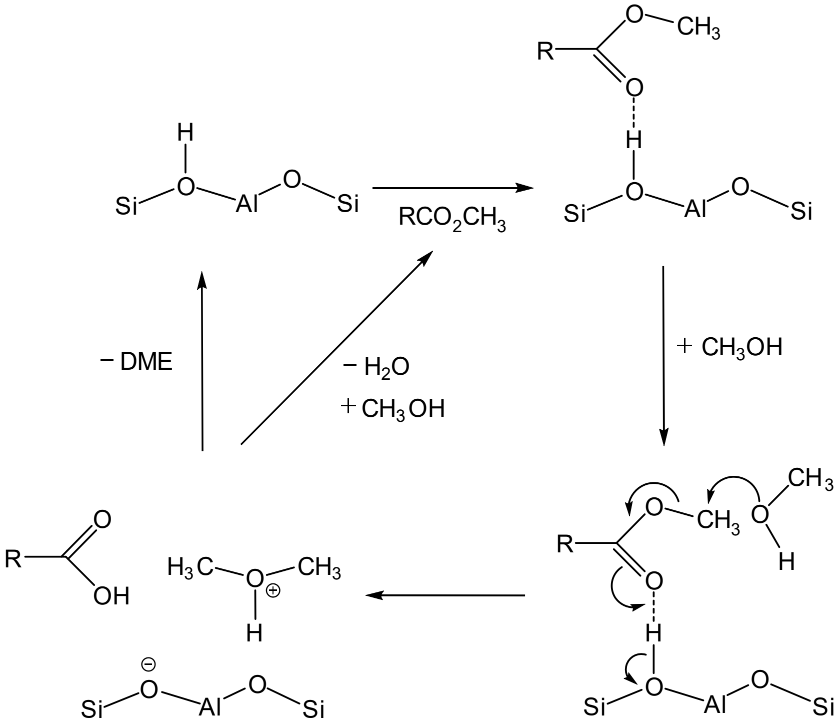

Figure 11. Indication of the reaction mechanisms of methyl ester promoted methanol dehydration to DME on zeolite.

4. Conclusions

Reaction kinetic, *in-situ* FT-IR and *in-situ* solid-state NMR spectroscopic techniques were performed to elucidate the promotional mechanism of methyl carboxylate esters in methanol dehydration to DME on zeolites. The reaction kinetic results indicate that the DME yield is dependent on both methanol and methyl *n*-hexanoate partial pressures across a range of temperatures (110 to 130 °C) studied. This is consistent with the promotional mechanism involving a bimolecular reaction between methanol and ester species adsorbed at the catalyst active sites. The *in-situ* FT-IR results reveal that methyl *n*-hexanoate can very rapidly titrate the Brønsted acid sites on H-ZSM-5 by adsorption through the ester carbonyl group. The methyl ester was found to be more strongly bonded to the Brønsted acid sites than methanol, which is consistent with the results of our previous adsorption energy calculations. In the *in-situ* NMR study, a much lower DME formation temperature (30 °C) was observed on the methyl *n*-hexanoate pretreated H-ZSM-5 samples, which further confirms the strong promotion by this methyl ester in methanol dehydration to DME. The adsorption and reactivity of methyl esters with different alkyl chain lengths on H-ZSM-5 indicates that surface methoxy species may not be important reaction intermediates for methyl ester promoted methanol dehydration to DME over zeolite catalysts, with a bimolecule associative mechanism playing a more important role.

5. Patents

A patent (WO2019/037764) is resulting from the work reported in this manuscript.

Author Contributions: Conceptualization, G.J.S.; investigation, Z.Y., B.J.D.-S., Z.X., Z.Z. and N.S.; writing—original draft preparation, Z.Y.; writing—review and editing, Z.Y., G.J.S., B.J.D.-S. and Z.X.; project administration, Z.Y., M.G., X.L. and G.H. All authors have read and agreed to the published version of the manuscript.

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