Probing direct carbon-carbon acylation of furans and long-chain acids over H-ZSM-5

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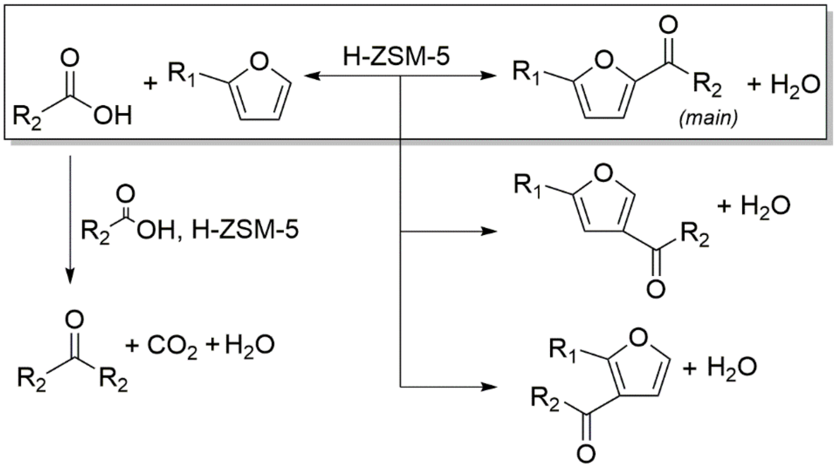
Abstract: The acylation of furan and 2-methylfuran (2-MF) with acetic acid (AA) and 1-hexanoic acid (HA) was studied over an H-ZSM-5 catalyst. Temperature-programmed desorption (TPD) measurements showed evidence that AA adsorbs strongly at Brønsted sites, with reaction to CO_2 and acetone beginning at 523 K, while both furan and 2-MF oligomerize upon adsorption at room temperature. Steady-state, flow-reactor measurements demonstrate that selectivities for the acylation reactions can approach 100% below 523 K when reactions are operated in excess organic acids, with maximum conversion limited by equilibrium. Coking becomes important when the reaction is operated in excess furan or 2-MF and at high reactant concentrations, while ketonization products are observed when the reaction is performed above 523 K. Potential uses for the reactions are discussed.



Reaction Scheme of Acylation and Observed Side Reaction

Keywords:

Acetic Acid; 1-Hexanoic Acid; Furan; 2-Methylfuran; H-ZSM-5; Acylation Reaction.

Introduction:

The acylation of furans with organic acids is potentially attractive for increasing the molecular weight of biomass-derived compounds in a controlled manner [1]. This could be employed for the production of fuels, where molecules larger than the six-carbon compounds produced from sugars would be useful [2]. Some of the products formed by acylation of furans could also find applications as intermediates for more valuable chemicals, such as pharmaceuticals and fragrances [3,4]. Finally, the acylation of furans with larger organic acids is an important step in the formation of a new class of tunable oleo-furan surfactants that has recently been reported [3]. These surfactants have the potential for replacing petroleum-based compounds with renewable chemicals that exhibit superior performance characteristics.

How to carry out the acylation reactions remains an important question. Friedel-Crafts acylation of aromatic compounds are classically performed using strong Lewis acids, such as $AlCl_3$, but these processes are not environmentally friendly and can produce side products that must be disposed of [5]. In the recent work on oleo-furan surfactants, the acylation reactions were carried out on zeolites with Brønsted acidity [3]. Although the conversions and selectivities in that work were good, the authors used the intermediate step of first forming the organic anhydrides [3]. It would be desirable to perform the reaction directly with the long chain organic acid using a heterogeneous, solid acid. Direct acylation of aromatics with acid has been demonstrated using H-ZSM-5 and H-BEA zeolite catalysts [1,6], with good selectivities, even in the presence of water. However, this previous study focused on understanding the reaction mechanisms and did not attempt to maximize the yields or determine the effect of different reactants.

It is instructive to consider an earlier study of the reaction between acetic acid (AA) and propene on H-ZSM-5 [7]. The reaction rates in that case were reasonably high at temperatures above 450 K, and the selectivities to the propyl acetates or their dehydration products were nearly 100% below 525 K. The catalyst was also stable at 475 K, with no observed deactivation over a period of 20 h. It is revealing that, in the absence of AA, propene reacts on H-ZSM-5 in this temperature range to form various oligomeric and cracking products [8]. Furthermore, the catalyst quickly deactivates during the reaction of pure propene under these conditions due to pore filling with oligomeric species. Apparently, the Brønsted sites are primarily populated by acetic acid during the reaction between AA and propene, greatly suppressing propene oligomerization. There are direct implications these result for acylation of furans, because furans can also oligomerize on strong Brønsted sites [9].

There are important differences between the acylation of furans and the reaction of AA with propene due to the large difference in gas-phase Proton Affinities (PA) between the furans and propene. Calorimetric measurements have shown that the stability of adsorption complexes at zeolite Brønsted sites scales well with PA [10]; and, based on PA, AA (PA=784 kJ/mol) is a stronger base than propene (752 kJ/mol), making it reasonable that it would compete favorably for sites. However, the PA of furan (803 kJ/mol) is slightly larger than that of AA and the PA of 2-MF (866 kJ/mol) is much larger. This would suggest that the selectivities for these two reactants might be very different from that of propene and from each other.

In the present study, we expanded the earlier work of Gumidyala, et al. [1] in order to more fully understand the effects of reaction conditions and reactants, particularly near equilibrium conversions. Comparisons were made for furan and 2-MF and for AA and 1-hexanoic acid (HA) as reactants. Because we found that H-ZSM-5 can be selective for these reactions, we restricted our studies to this catalyst. Major conclusions are that the maximum yields are largely limited by equilibrium for temperatures below about 523 K, and that catalyst stability requires operating in excess organic acid.

Experimental Techniques:

The H-ZSM-5 catalyst used in this study was obtained from Zeolyst (CBV5524G, SiO_2/Al_2O_3 =50). It was in the ammonium-ion form as received and converted to the acidic form by heating in dry, flowing air to 823 K for 6 h. This zeolite has been used in other studies from our laboratory, where its properties were described in more detail [11]. Based on Temperature-programmed-desorption/thermogravimetric-analysis (TPD-TGA) measurements with 2-propanamine [12], its Brønsted-site density is approximately 500 μmol/g, a value somewhat less than the Al concentration of 625 μmol/g. A purely siliceous MFI zeolite, SiZSM-5, also described in previous papers as “ZSM-5(F, Si)” [11], was used for some adsorption studies in order to confirm the effect of Brønsted sites on adsorption. The chemicals in this study were used as received: 2-MF (99%, contains 200-400 BHT as stabilizer) and HA (≥99.5%) are from ALDRICH; furan (99+%) is from ACROS ORGANICS; AA (certified ACS) is from Fisher Chemical.

TPD-TGA measurements were performed on 50-mg samples placed in the sample pan of a CAHN 2000 microbalance [11], which could be evacuated to ~10^{-7} torr using a diffusion pump. After heating the sample in vacuum to 823 K, the sample was cooled to room temperature, exposed to vapor from the adsorbate of interest, and evacuated for 1 h. Desorption measurements were performed by heating the sample at 10 K/min while measuring the partial pressures with an SRI quadrupole mass spectrometer (RGA100).

A tubular reactor, operating at 1-atm total pressure, was used in the steady-state reaction measurements. The reactor was a 200-mm long stainless steel tube with a 4.6-mm inside diameter [13]. The zeolite samples (200-mg in most cases) were pressed into thin wafers, which in turn were broken into small pieces and loaded into the center of the tube. Glass wool was placed on both sides of the catalyst bed, and the bed was held in place by inserting a solid stainless-steel rod into the end of the tube. The rod also reduced the empty volume in the reactor, decreasing the hold-up of products. The reactants were well mixed and fed to the reactor using syringe pumps (PHD 2000 Infusion, Harvard Apparatus), with 20-mL/min helium added as a carrier. All of the reaction lines were wrapped with heating tape and held at a temperature at least 50 K higher than the condensation temperature of the highest boiling reactant. The products were measured using an on-line gas chromatograph (Buck Scientific) equipped with a capillary column (HP-INNOWAX, Agilent Technologies) and identified from the retention times, calibrated using a GC-Mass Spec (QP5000, Shimadzu) with the same column. Calibration of the GC for the acylation products formed by AA was performed using compounds purchased from Sigma-Aldrich. Because the products formed by reaction of the furans with HA were not commercially available, we assumed that the GC sensitivities were the same as those of the corresponding AA products.

Throughout this manuscript, conversions are defined as the fraction of the entering reactant that forms product before leaving the reactor, and selectivities are defined as the fraction of reacting molecules that form the desired product.

Results:

Adsorption Studies

The adsorption of AA in H-ZSM-5 was studied in some detail previously [14], but TPD-TGA measurements, shown in Figure 1(a), were repeated here. Following room-temperature adsorption and 1-h evacuation, the coverage was still about 1000 μmol/g, well above the Brønsted-site density of 500 µmol/g (the main peak in the mass spectrum is at m/e = 45, with small contributions at m/e = 18 and 44). Roughly half of the adsorbed AA desorbed below 400 K, leaving a coverage close to that of the Brønsted-site density. An inflection point in both the TGA and the m/e=45 TPD signals at just above 400 K also suggests formation of an adsorbed species with a coverage close to one molecule per site. Above 400 K, additional AA desorbs intact until 500 K, when mass spectra of the desorbing products change rather dramatically. The peaks at m/e = 44 and 58, representing primarily CO_2 and acetone, respectively, are formed above 500 K due to ketonization of acetic acid. Acetone is highly reactive at acid sites at relatively high temperature [15], other products are likely formed by secondary reactions but not reported here, since it is beyond the temperature range we care about, to be discussed later. It is noteworthy that a similar light-off temperature for reaction of AA to other products was observed in flow-reactor measurements [16].

TPD-TGA results for furan on H-ZSM-5 are shown in Figure 1(b), with results that are very similar to those reported previously for 2,4-dimethylfuran on an acidic H-BEA zeolite [9]. Following room-temperature exposure and 1-h evacuation, the coverage of furan remains over 750 µmol/g, well above the Brønsted-site density. However, unlike AA which tends to form relatively strong hydrogen bonds with even siliceous materials, physically adsorbed furans are easily removed from siliceous zeolites [9]. This is shown by the TGA data for furan in SiZSM-5, also reported in Figure 1(b), which demonstrate that essentially all of the furan could be removed by evacuation. The fact that the coverage of furan on H-ZSM-5 was greater than one per site after evacuation likely implies that some of the furan had undergone oligomerization at the Brønsted sites, even at room temperature. In TPD, nearly half of the furan leaves the zeolite below 500 K, with the rest desorbing as a range of other products formed by oligomerization and cracking at higher temperatures. Adsorption of 2-MF in H-ZSM-5 gave similar results as that for furan, as shown in Figure 1(c). The initial coverage of 2-MF after evacuation, greater than 1000 µmol/g, was more than twice the Brønsted-site density, implying that the extent of oligomerization might be slightly higher than that of furan. Again, some of the 2-MF desorbed intact during TPD, possibly by dissociation of dimers, but more than half desorbed as products that we could not identify with the mass spectrometer.

Reaction of AA with 2-MF and Furan

An initial indication of the temperature dependence of the reaction between furan and AA is shown in Figure 2. For these measurements, the flow rates and reactant concentrations were fixed, while the conversions and selectivities were measured as a function of temperature between 473 and 573 K. As will be shown later, catalyst stability and reaction selectivities were improved in excess AA; therefore, this set of experiments was performed with an AA:furan ratio of five, in 95-mol% He. The H-ZSM-5 catalyst was held in the flowing reaction mixture at each temperature for at least two hours, and there was no evidence for deactivation over the course of the measurements under these conditions. The data show that the AA conversion increases steadily with temperature, while the furan conversion goes through a maximum at about 523 K. Because there is a rapid increase in the formation of CO_2 and acetone from AA above this temperature, the decrease in conversion of furan must be related to the ketonization reaction of AA at the acid sites. This implies that the ketonization reaction is in competition with the acylation reaction and not part of the mechanism for acylation. The selectivity for furan forming 2-acetylfuran was 100% at all temperatures, within our ability to detect the products.

The analogous results for acylation of 2-MF, shown in Figure 3, are nearly identical to that for furan. The conversion of AA again increases steadily, with CO_2 and acetone appearing in the products beginning at 548 K. As with furan, the conversion of 2-MF goes through a maximum at 523 K, and the selectivity to acylation products is again 100%. The one difference with 2-MF was that there was a significant shift towards the 2,3-methyl-acetylfuran and 2,4-methyl-acetylfuran isomers from the 2,5-methyl-acetylfuran with increasing temperature.

Figure 4 shows the effect of changing the AA:2-MF feed ratio. These experiments were performed at 523 K, again with dilution in 95-mol% He. Because the catalyst was not stable in excess 2-MF, the measurements were performed within 10 minutes of introducing the feed, and the catalyst was replaced after each run. A most significant observation was that higher molecular-weight products, primarily 2-MF dimers, were observed when the AA:2-MF ratio was less than one. Furthermore, the carbon balance was, within experimental error, 100% for AA:2-MF ratios above one but became much worse at lower ratios. The poor carbon balance at low AA:2-MF ratios is primarily due to coke deposition in the catalyst, since catalyst deactivation became appreciable at low ratios. For example, as Figure 4(b) shows, when the AA:2-MF ratio was 0.2, the 2-MF conversion dropped from 50% to 40% after 100-min time on stream, while rates were completely stable at high AA:2-MF ratios. Finally, Figure 4 shows that the 2-MF conversion went through a minimum at intermediate AA:2-MF ratios. The higher conversion at low ratios was due to oligomerization of the 2-MF, while the higher conversion at the highest ratio was simply due to the fact that the amount of 2-MF in the feed is less.

Figure 5 shows the effect of He dilution for reaction of AA and 2-MF, for a fixed AA:2-MF ratio of 5 at 523 K. Increasing the feed concentration to 10% did not change the conversion, but removing He entirely caused the conversion to decrease significantly, from roughly 30% to 12.5%. Furthermore, increasing the reactant concentration decreased the catalyst stability, with the conversion dropping from a value of 23% after 30 min time on stream to 6% after 150 min. The selectivity for acylation products decreased as well, with the formation of higher molecular weight products.

Because the acylation reactions are expected to be reversible, the conversions reported here are likely to be at least partially limited by equilibrium. To determine whether this was the case, we measured the conversions of both 2-MF and furan in their reactions with AA as a function of reactor space time. The measurements were performed at 523 K, with 95% dilution in He and a AA:furan(2-MF) of five in order to avoid coking issues. This data is shown in Table 1. For both reactants, the conversion stopped increasing above a certain residence time, implying that equilibrium had been reached. The equilibrium constants at 523 K were calculated to be 0.041 for the reaction of AA with furan and 0.075 for the reaction of AA with 2-MF. To confirm that these were equilibrium values, we also performed experiments in which water was added to the feed, the corresponding equilibrium constants calculated from different water ratios in the initial feed were unchanged, as shown in Table 2.

Reaction of 2-MF with Hexanoic Acid (HA)

To determine whether a similar approach could be used to react larger organic acids with the furans, we next performed the reaction HA with 2-MF. Because HA has a lower vapor pressure, the experiments were performed using 95-mol% n-hexane as the diluent in place of He. This allowed the reactants to be fed as a liquid mixture directly into the reactor using a syringe pump. The reaction was performed at 1.0 atm and the HA:2-MF ratio was again fixed at five. The reaction was monitored using a fixed feed flow rate, while measuring the conversion and product distribution as a function of the reaction temperature, starting from 473 K, a temperature at which all of the reactants and products will be in the vapor phase. We observed no changes in the conversions with time, showing that the catalyst was again completely stable under the conditions of these experiments. Figure 6 demonstrates that the trends in conversion and selectivity were similar to what we observed for reaction of AA with 2-MF. The conversion of 2-MF again appears to reach a maximum of about 32% at 523 K; and the ketonization product for HA, 6-undecanone, was observed starting at 548 K. While the 2-MF selectivities for forming the Friedel-Crafts products were 100% under these conditions, significantly more of the 3,5- and 4,5-products were observed with HA. The conversion was again found to reach a maximum with increasing space time (Table 1) and the equilibrium constant at 523 K was calculated to be 0.036.

Discussion

In the present work, we confirmed results from previous studies which showed that high selectivities could be achieved in the Friedel-Crafts reaction of organic acids and furans using the Brønsted acid sites in siliceous zeolites [1]. Unfortunately, equilibrium limited the ultimate yields, but selectivities can approach 100%. If methods are developed to remove the water selectively from the reaction mixture, it may be possible to increase the yields to significantly higher levels.

Although we cannot completely rule out the possibility that the reaction occurs through the formation of stable acyl groups, we believe the data suggest that the reaction proceeds through a bimolecular process involving the molecular organic acid and furan (or 2-MF) at the Brønsted sites. Previous work had shown that stable acyl groups can be formed in H-ZSM-5, since mild heating of adsorbed acetyl chloride produces HCl and an adsorption complex with similar vibrational and ^{13}C NMR characteristics to acetic acid [14]. However, if long-lived acyl groups had been formed from adsorbed acetic acid at temperatures below that at which reaction occurs, we should have observed water desorption in TPD at temperatures below that at which reaction occurs. Instead, the reaction products from TPD of acetic acid showed only molecular acetic acid at temperatures where the reaction is highly selective. Formation of CO_2 and acetone, due to the ketonization reaction, are formed at higher temperatures; but it is significant that the onset temperature for CO_2 in TPD occurs at the same temperature at which selectivity for acylation decreases and ketonization products form in the steady-state reaction. This implies that the ketonization reaction is a competing reaction and probably not associated with the desired reaction route.

Catalyst coking was an issue in excess furan (2-MF) and at higher reactant concentrations. Both of these observations are consistent with oligomerization of furan at the Brønsted sites, which was also observed in the adsorption studies. It is perhaps more surprising that oligomerization was not a significant problem when the reaction was performed in excess acid given that oligomerization of furan appears to occur at room temperature in adsorption studies. This is an important clue as to what is the primary species populating the Brønsted sites under reaction conditions. As discussed in the Introduction, heats of formation of adsorption complexes in H-ZSM-5 scale reasonably well with Proton Affinities (PA) [10]; based on this, the furans would be expected to compete favorably with organic acids for Brønsted sites. However, calorimetric measurements have also shown that hydrogen-bonding contributions can further stabilize adsorption beyond that predicted from simple PA correlations. For example, the heats of adsorption for alcohols at Brønsted sites in H-ZSM-5 are larger than one observes for nitriles that have similar PA, likely due to these hydrogen-bonding contributions [17]. The fact that acetic acid desorbs at higher temperatures than the furans in TPD, Figure 1, also implies that the organic acids are bound to the Brønsted sites with at least comparable energetics. However, it is also possible that the sites are primarily populated with furans and that oligomerization is simply prevented by physically-adsorbed, organic-acid molecules blocking a second furan molecule from approaching the acid sites. Whatever the mechanism, the fact that the organic acids prevent oligomerization of the furans is interesting and consistent with results from the previous study of acetic acid reactions with propene [7].

In summary, the high degree of control for making higher molecular weight products makes this an attractive approach for producing useful chemicals from biomass sources. Additional research to more fully understand these reactions is worthwhile.

Acknowledgements

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Conclusions:

The acylation of furan and 2-methylfuran with acetic acid and 1-hexanoic acid can be performed with moderate selectivity on an H-ZSM-5 zeolite. Conversions are limited by equilibrium, and reaction temperatures should be maintained below 523 K to avoid ketonization products. Coking due to oligomerization of the furans can occur when the reactions are carried out in excess furans.

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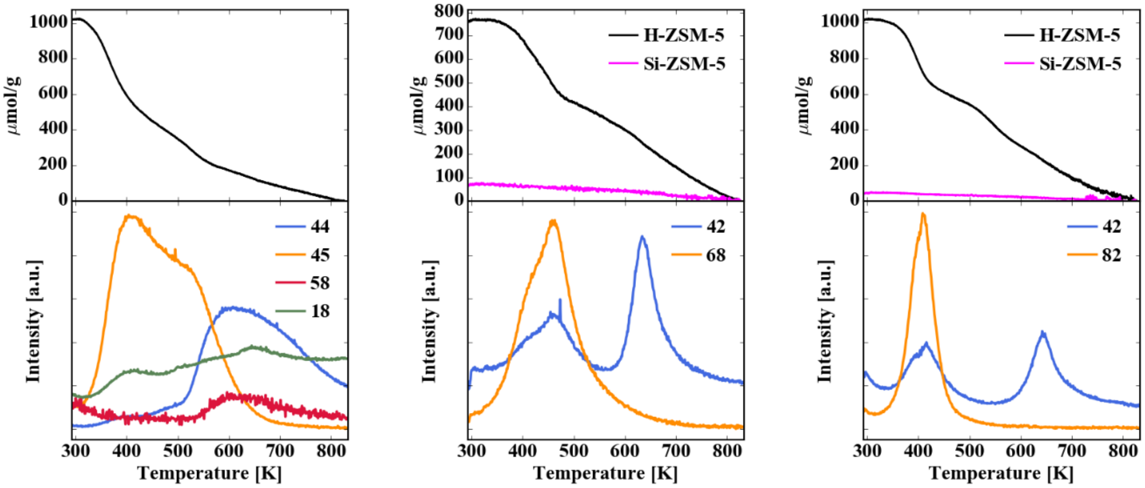
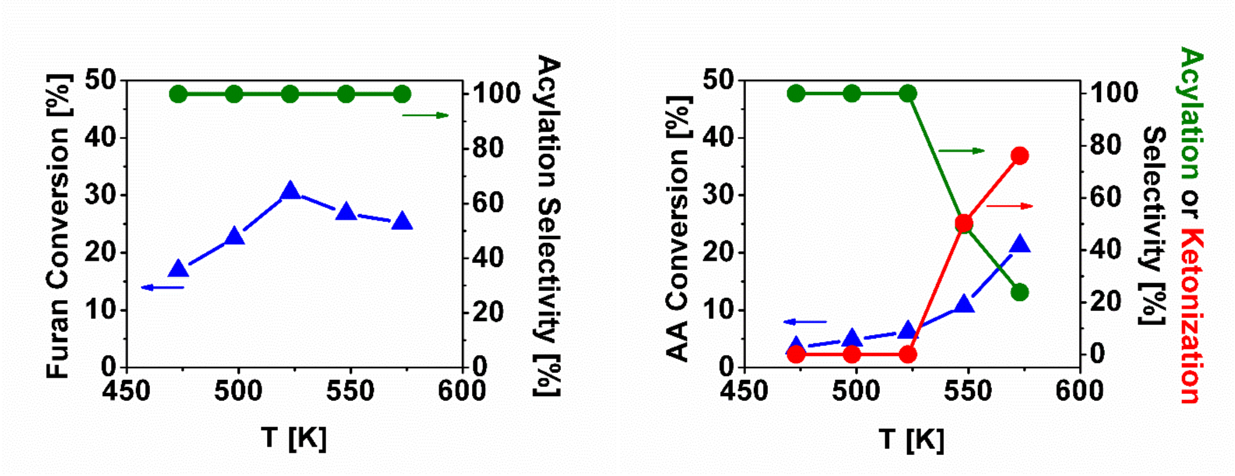


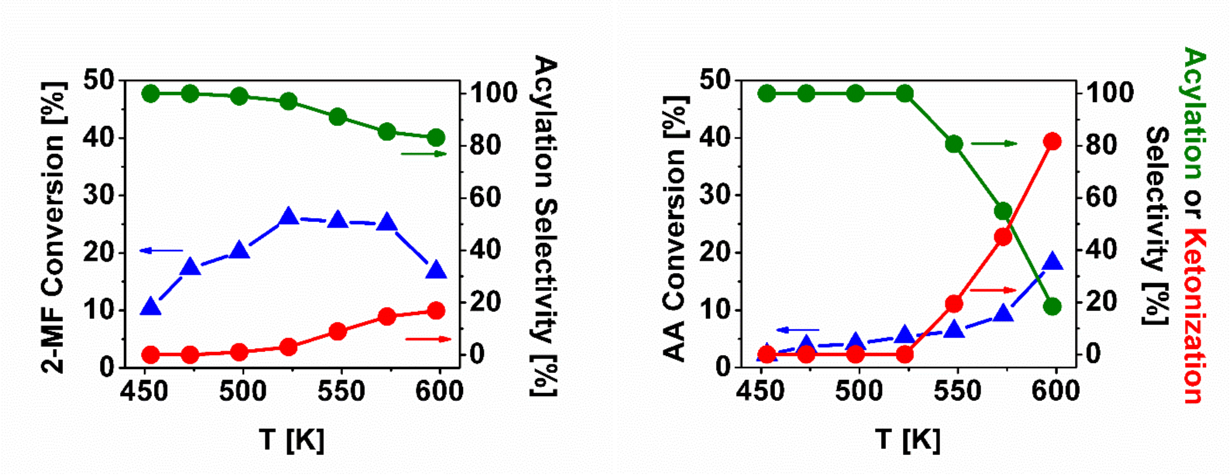
(a) (b) (c)

Figure 1. Temperature Programmed Desorption - Thermogravimetric Analysis. TPD-TGA of **(a)** acetic acid on H-ZSM-5; **(b)** furan on H-ZSM-5; **(c)** 2-methylfuran (2-MF) on H-ZSM-5. TGA results for furan and 2-MF on SiZSM-5 are also shown in (B) and (C). The TPD peaks correspond to CO_2 (m/e = 44), AA (m/e = 18, 45), acetone (m/e = 58), furan (m/e = 68), 2-MF (m/e = 82), oligomers (m/e = 42), water (m/e = 18).



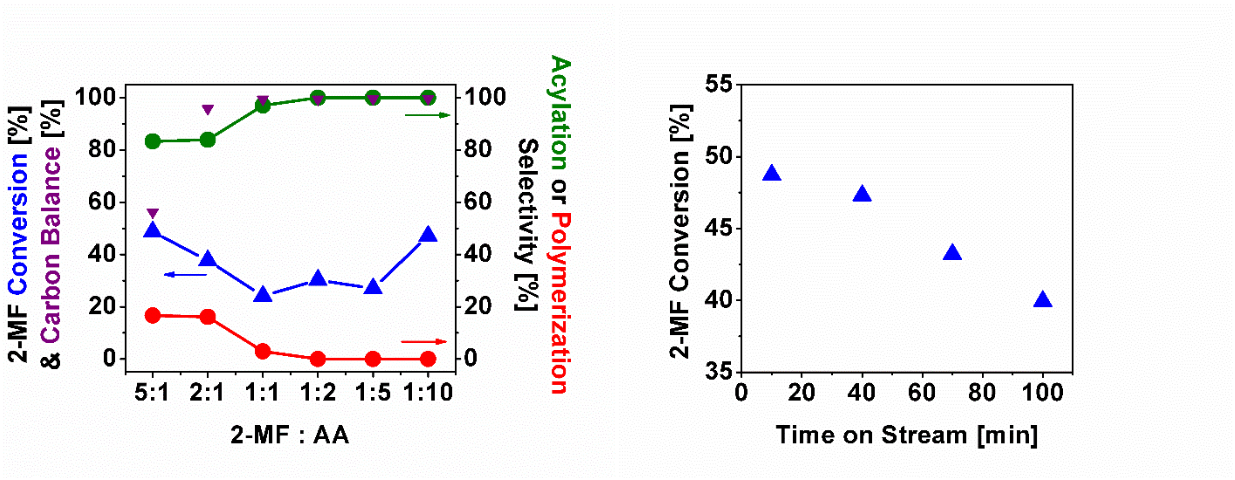
(a) (b)

Figure 2. Temperature dependence for the **(a)** conversion (blue) and selectivity (green: 2-acetylfuran) of furan and for the **(b)** conversion (blue) and selectivity (green: acylation; red: ketonization) of acetic acid (AA) in the reaction of AA with furan, using an AA:furan ratio of 5, in 95-mol% He.



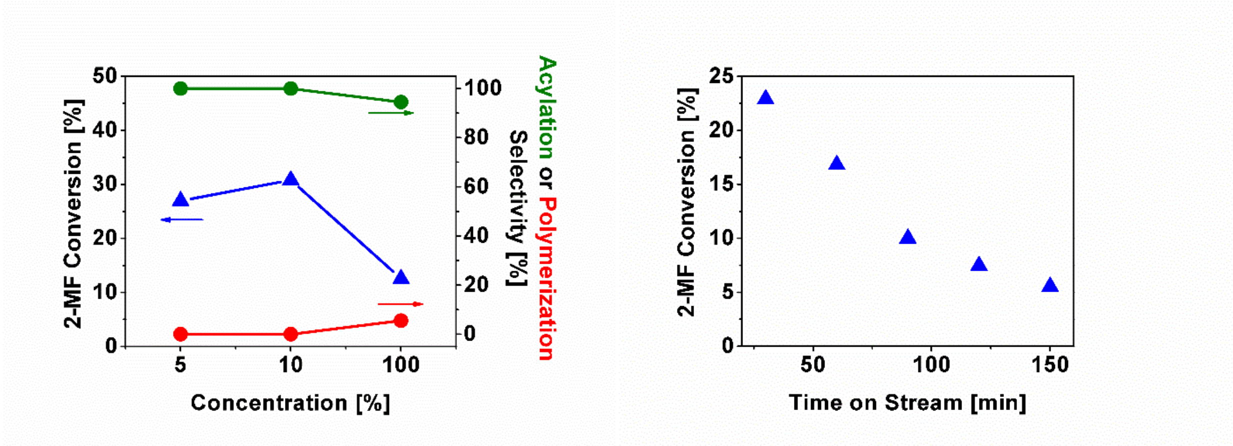
(a) (b)

Figure 3. Temperature dependence for the **(a)** conversion (blue) and selectivity (green: 2-acetyl-5-methylfuran; red: 3-acetyl-5-methylfuran and 4-acetyl-5-methylfuran) of 2-MF and for the **(b)** conversion (blue) and selectivity (green: acylation; red: ketonization) of acetic acid (AA) in the reaction of AA with 2-MF, using an AA:furan ratio of 5, in 95-mol% He.



(a) (b)

Figure 4. (a) 2-methyl-furan (2-MF) conversion (blue) and selectivities (green: acylation products, include isomers; red: high-molecular-weight products) for reaction of acetic acid (AA) and 2-MF as a function of the 2-MF:AA feed ratio at 523 K, with 95-mol% He balance. The carbon balance is also shown (purple, down triangle). **(b)** Conversion of 2-MF as a function of time for an 2-MF:AA ratio of 5.



(a) (b)

Figure 5. (a) Conversions (blue) and selectivities (green: acylation products, include isomers; red: high-molecular-weight products) for the reaction of acetic acid (AA) and 2-methyl-furan (2-MF) as a function of feed concentration (balance He). The 2-MF:AA ratio was 0.2. **(b)** Conversion of 2-MF as a function of time for pure feed with an 2-MF:AA ratio of 0.2.

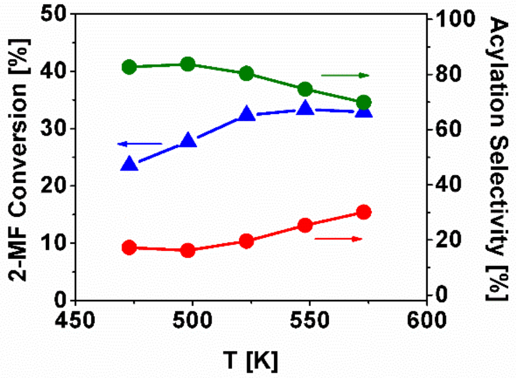


Figure 6. Temperature dependence for 2-methyl-furan (2-MF) conversion (blue) and selectivities (green: 2-hexanoyl-5-methylfuran; red: 3-hexanoyl-5-methylfuran and 4-hexanoyl-5-methylfuran) during reaction of hexanoic acid (HA) with 2-MF using an HA:2-MF ratio of 5 with 95-mol% He.

Table 1. Effect of contact time on conversions for the reaction of acetic acid (AA) and hexanoic acid (HA) with 2-methylfuran (2-MF) and furan at 523 K.

Reactants	WHSV[h^{-1}]	Conversion: 2MF or furan	Equilibrium Constant*
2-Methylfuran + Acetic Acid	0.82	33.6%	
	0.41	39.3%	
	0.21	43.5%	
	0.16	43.2%	
	0.10	43.8%	0.075
Furan + Acetic Acid	0.40	34.8%	
	0.20	34.5%	
	0.10	35.0%	0.041
2-Methylfuran + 1-Hexanoic Acid	0.15	32.4%	
	0.09	32.3%	
	0.03	33.4%	0.036

$$* \, Equilibrium\ constant \equiv \frac{[Acylation\ Product][H2O]}{[Furan\ or\ 2{-}MF][AA\ or\ HA]}$$

Table 2. Effect of water addition on conversions for the reaction of acetic acid (AA) with 2-methylfuran (2-MF) at 523 K at low WHSV.

Acetic Acid : 2-Methylfuran : H_2O	**Conversion of 2-MF**	**Corresponding equilibrium constant**
5:1:0	43.5%	0.073
5:1:0.5	29.4%	0.070
5:1:1	22.0%	0.072