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The acylation of propene by acetic acid over H-[Fe]ZSM-5 and H-[Al]ZSM-5

O. Kresnawahjuesa[a], R.J. Gorte[a,*], David White[b]

[a] *Department of Chemical & Biomolecular Engineering, University of Pennsylvania, 311 Towne Building, 220 South 33rd Street, Philadelphia, PA 19104, USA*
[b] *Department of Chemistry, University of Pennsylvania, 311 Towne Building, 220 South 33rd Street, Philadelphia, PA 19104, USA*

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Abstract

We have studied the vapor-phase reaction of acetic acid with propene over H-[Al]ZSM-5 and H-[Fe]ZSM-5 molecular sieves between 425 and 600 K, for acetic acid partial pressures of 0.033–0.066 Bar, with propene:acetic acid ratios between 1 and 4. Reasonable conversions were obtained above 450 K. Both H-[Fe]ZSM-5 and H-[Al]ZSM-5 showed high activities at 450 K, with selectivities to propyl acetates of ∼90% using a propene:acetic acid ratio of 2 and ketones formed by dehydration of the acetates making up most of the remaining products. The reaction rate was completely stable at 450 K for at least 20 h, and the product distribution was insensitive to the reactant feed ratio for a propene:acetic acid ratio above 2. On H-[Fe]ZSM-5, dehydration of the acetates became increasingly important at higher temperatures, with the selectivity to ketones approaching 80% at 525 K. At still higher temperatures, reaction pathways that did not involve propyl acetates became important. The high selectivity for forming propyl acetates and the absence of olefin oligomerization is believed to result from having the acid sites occupied (saturated) by acetic acid. Finally, the acid-site density measured on H-[Fe]ZSM-5 after weeks of catalyst testing remained the same as the initial site density, showing that this material has sufficient stability for fine-chemicals synthesis.

Keywords: Acetic acid; Propene; Propyl acetate; H-ZSM-5; H-[Fe]ZSM-5; Brønsted acidity

1. Introduction

Sheldon and Downing [1] have pointed out that solid acids are not often used in fine-chemicals synthesis, even though there could be significant advantages to practicing these reactions over solid acids due to environmental concerns associated with high levels of waste in many homogeneous processes. There are a number of reasons that zeolites are not commonly used, including the fact that synthetic-organic chemists have not traditionally used heterogeneous catalysts and the fact that the small-scale operations of the fine-chemicals industry make the costs of developing new processes difficult to recoup. However, there have also been more fundamental difficulties associated with replacing homogeneous acids on a wide scale.

Attempts to replace homogeneous acids with their heterogeneous counterparts in fine-chemicals synthesis have met with some success, as demonstrated in recent review articles [1–4]. For example, it has recently been reported by Rhodia that a commercial process has been developed for the reaction of anisole to para-acetoanisole using acetic anhydride as the acylating agent and an acidic zeolite as the catalyst in a fixed-bed reactor [5]. Rhodia reports that the new process results in a significant reduction in both operating costs and unwanted effluents, as well as an increase in selectivity to the para isomer products. The gas-phase acylation of benzene with acetic acid has also been claimed [6], although others have stated that “little success has been achieved with substrates such as toluene and benzene” [7]. From the significant literature on reaction measurements for the acylation of anisole [7–13], phenol [14–16], and other aromatics [17–20] and olefins [21,22], it is clear that there are problems with catalyst deactivation and selectivity issues, particularly with olefinic reactants [21,23–25].

Deactivation is usually associated with the formation of high molecular weight products (coking) that block adsorption of reactants at the acid sites. For example, we have shown that both propene and 1-butene oligomerize

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[*] Corresponding author. Tel.: +1-215-898-4439; fax: +1-215-573-2093.
E-mail address: gorte@seas.upenn.edu (R.J. Gorte).

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rapidly on the acidic zeolite, H-[Al]ZSM-5, at room temperature [23,25]. Furthermore, when the oligomers formed in H-[Al]ZSM-5 are decomposed by heating in vacuo, aromatic products are formed, providing evidence that hydride-transfer reactions, which can ultimately lead to catalyst coking, occur very readily under mild conditions [23]. It is possibly significant that oligomerization of propene occurs only at higher temperatures on H-[Fe]ZSM-5, the siliceous molecular sieve in which acid sites are generated by framework Fe^{3+} [23,24]. Furthermore, hydride-transfer reactions were virtually eliminated on H-[Fe]ZSM-5 [23]. Obviously, selective, stable operation of a reaction involving olefin reactants must minimize oligomerization and avoid hydride transfer.

In the work to be discussed in the present paper, we set out to investigate one of the simplest acylation reactions, the reaction between acetic acid and propene, on H-[Al]ZSM-5 and H-[Fe]ZSM-5. The product of this reaction, propyl acetate, is of commercial interest as a solvent for paints and similar applications; it is typically formed by the reaction of acetic acid with propyl alcohol in aqueous solutions [26]. We had expected that the selectivity for the acylation of propene would be poor in H-[Al]ZSM-5 due to the tendency of propene to oligomerize in this solid acid and that a higher selectivity might be observed in H-[Fe]ZSM-5. While H-[Fe]ZSM-5 does show higher selectivity to acylation products at higher temperatures, we find that both acidic solids show excellent stabilities and reasonably high selectivities at 450 K, in excess propene, with ketones formed by dehydration of the propyl acetates being the primary side products. At temperatures below ∼500 K, we found no evidence for olefin oligomerization in the products. In this manuscript, we will discuss the experimental data and suggest reasons for the surprisingly good performance.

2. Experimental

Two molecular-sieve samples were used in this study. The H-[Al]ZSM-5 sample was obtained from NIST in the ammonium-ion form and was reported to have $Si/Al_2 = 60$. It was placed in the acidic form by simply heating it in flowing dry air in the tubular reactor (2.54 cm i.d.) at 773 K for 4 h before exposing it to reactants. The Al-free ferrosilicate, [Fe]ZSM-5, was synthesized and characterized according to procedures described elsewhere [23,27]. The sample was characterized by XRD, which showed that the sample had the MFI structure with a lattice parameter that agreed with the targeted framework Si/Fe_2 of 60. To place the sample in its acidic form, the [Fe]ZSM-5 was calcined in flowing air at 750 K for 4 h and ion exchanged with 0.1 M NH_4Cl at 345 K, three times (∼1 h each). Between each ion-exchange, the sample was washed with distilled water until no Cl^- was detected by $Ag(NO_3)$ solution on the filtrate. The crystallite sizes of H-[Al]ZSM-5 and H-[Fe]ZSM-5 were determined to be 0.5 and 10 μm, respectively, by scanning electron microscopy.

The Brønsted-acid site densities of each sample were obtained from simultaneous temperature-programmed-desorption (TPD) and thermogravimetric-analysis (TGA) measurements following isopropylamine adsorption. In this technique, the Brønsted-acid site density is determined from the amount of propene and ammonia that form by decomposition of the alkyl ammonium ion between 575 and 650 K [28–31]. The initial Brønsted-site density of each sample was determined to be 500 μmol/g, in reasonable agreement with its framework Al and Fe concentrations. After 250 h of reaction at temperatures between 450 and 600 K, the site density of H-[Fe]ZSM-5 sample was tested again and shown to remain high, 475 μmol/g, suggesting that catalyst deactivation of the solid acid under reaction conditions is insignificant. Because we had anticipated that coking would be a problem with H-[Al]ZSM-5 due to oligomerization reactions with propene [23], most of our experiments were performed on the H-[Fe]ZSM-5 sample. However, later experiments with H-[Al]ZSM-5 showed that the two samples had similar activities, selectivities, and stabilities, at least at 450 K, so that most of the results that will be reported were obtained on H-[Fe]ZSM-5.

The reaction of acetic acid and propene was carried out in a fixed-bed, up-flow, glass reactor (0.64 cm i.d.) at atmospheric pressure, using between 2.3 and 2.4 g of catalyst. (Measurements were also performed without catalyst on an empty glass tube with glass wool to check for gas-phase reactions, but no products were observed using any of the conditions in this study.) Acetic acid was fed to the reactor by bubbling He through the liquid, using the temperature of the liquid to control the partial pressure. The mixture of He and acetic acid was then mixed with propene and fed to the reactor. The total flow rate of He, acetic acid, and propene was maintained at 50 ml/min. The partial pressure of propene was allowed to range from 0.066 to 0.146 Bar, while the partial pressure of acetic acid was varied between 0.033 and 0.066 Bar. The weight hourly space velocity was maintained at $\sim 4.7\,h^{-1}$ for all reactions. The effluent from the reactor passed through a gas-sampling valve, which allowed the products to be analyzed with a Shimadzu GCMS-QP5000 equipped with Alltech capillary column EC-1000.

The conversion of propene and acetic acid were calculated according to the following equations:

$$x_{C_3H_6\ \text{or}\ CH_3COOH}(\text{mol\%}) = \frac{\text{moles of } C_3H_6 \text{ or } CH_3COOH \text{ reacted}}{\text{moles of } C_3H_6 \text{ or } CH_3COOH \text{ fed}} \times 100 \qquad (1)$$

The selectivity of various products coming out of the reactor was calculated as follows:

$$S_i(\text{mol\%}) = \frac{\text{moles of product } i \text{ produced}}{\text{moles of acetic acid reacted}} \times 100 \qquad (2)$$

The selectivity and conversion data reported in the figures and table in this paper are the steady state values, typically obtained after 350–400 min of reaction time.

3. Results

Fig. 1 summarizes the reactions that occur between acetic acid and propene on both H-[Al]ZSM-5 and H-[Fe]ZSM-5. The primary products formed at 450 K in excess propene are *n*-propyl and iso-propyl acetate; however, these acetate products also undergo dehydration to form their respective ketones, iso-propyl acetate forming 3-methyl-3-butene-2-one and *n*-propyl acetate forming 3-penten-2-one. In parallel to the desired bimolecular reactions between acetic acid and propene are the undesirable side reactions. Acetic acid can react to form acetone and CO_2 [32–37]; olefins and ketones can undergo oligomerization and cracking to form a wide range of products [23,38].

Table 1 summarizes the conversions and selectivities observed on 2.4 g of H-[Fe]ZSM-5 or H-[Al]ZSM-5 at 450 and 525 K, for a feed composition of 0.04 Bar of acetic acid and 0.08 Bar of propene, balanced with He carrier gas to achieve a total flow rate of 50 ml/min. The results for both catalysts are similar and demonstrate that the reaction at both temperatures proceeds mainly through the primary reaction pathway. The slightly higher conversions observed on H-[Al]ZSM-5 could be due to the stronger sites on this

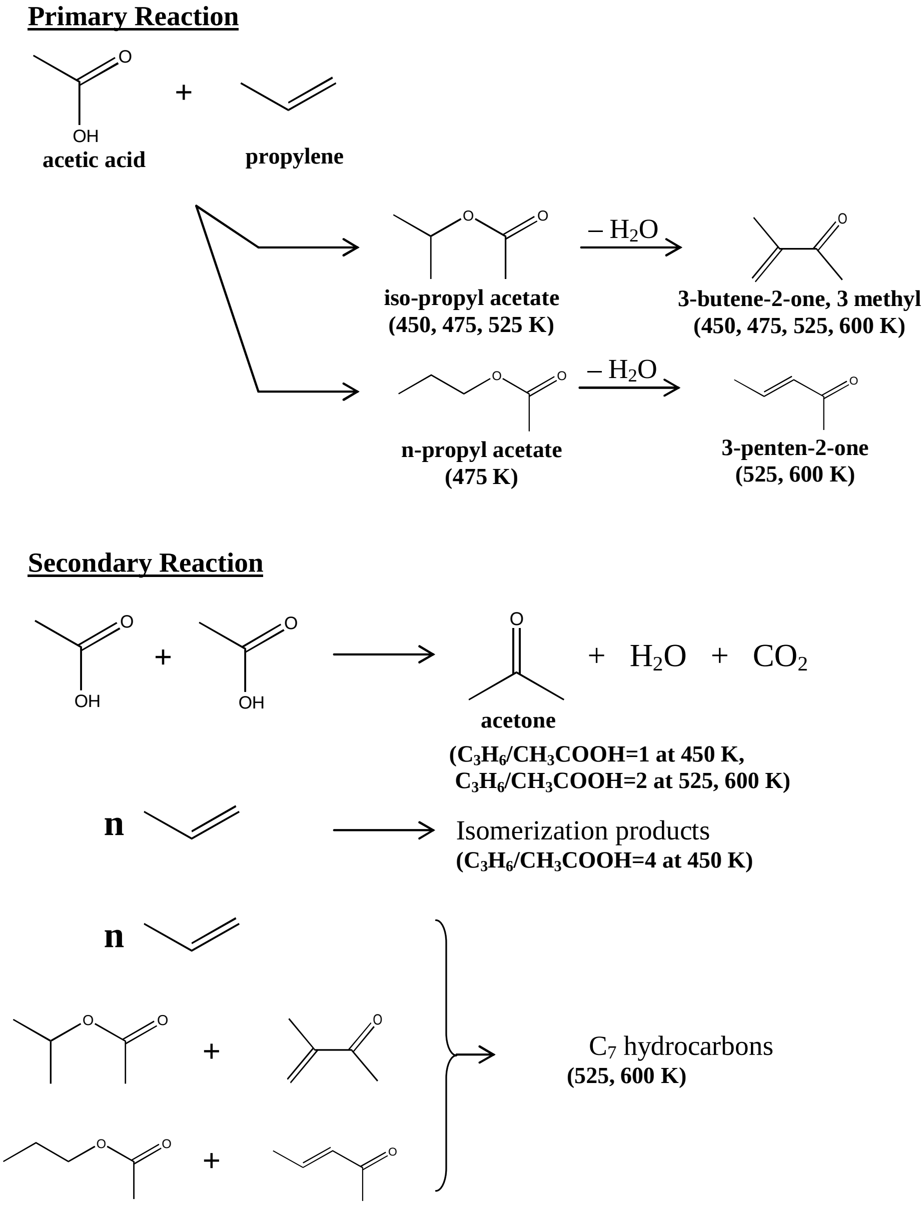

Fig. 1. Reactions of propene and acetic acid over the solid acids used in this study. The information in the bracket indicates the reaction conditions at which these products were observed.

Table 1
Comparison of catalytic activity of H-[Al]ZSM-5 and H-[Fe]ZSM-5 for propylene with acetic acid reaction at different temperatures

Performance (%)	450 K		525 K	
	H-[Al]ZSM-5	H-[Fe]ZSM-5	H-[Al]ZSM-5	H-[Fe]ZSM-5
Acetic acid conversion	13 ± 2	11 ± 2	19 ± 2	16 ± 2
Propene conversion	6.9	5.5	5.2	7.9
Acetate products[a] selectivity[c]	90	92	5.0	5.8
[$i/(i+n)$ Propyl acetate ratio]	0.96	0.98	1	1
Ketone products[b] selectivity[c]	9.7	8.0	82	70

Propylene partial pressure: 0.08 Bar, acetic acid partial pressures: 0.04 Bar, reactants total flow rate: 50 ml/min and catalyst weight: 2.35 g.

[a] Acetate products consist of isopropyl acetate and *n*-propylacetate.

[b] Ketone products consist of 3 methyl 3-buten-2-one and 3-penten-2-one.

[c] Product selectivity is calculated with respect to the amount of acetic acid reacted (Eq. (2)).

material, but could also be due to the differences in the crystallite size of the two samples because the selectivities on the two molecular sieves were virtually identical. At 450 K, the selectivity of the acetate products with respect to acetic acid reacted is nearly 90%, with the ketones, formed via a mechanism similar to aldol dehydration, making up most of the remaining products. At 525 K, side reactions become more important, as indicated by the fact that the selectivities to acetate and acetate-dehydration products no longer sum to 1. Also, on H-[Al]ZSM-5, the amounts of acetic acid and propene that react are no longer equal at the higher temperature. The major difference at 525 K, however, is that the ketones formed by acetate dehydration dominate at the higher temperature.

We chose to further characterize the reaction using H-[Fe]ZSM-5, since the results in Table 1 suggest that the results for H-[Al]ZSM-5 would likely be similar. Fig. 2 reports the effect of changing the reaction temperature on the conversions of both propene and acetic acid and on the selectivities to acetates, ketones, and higher molecular-weight products, calculated based on the amount of acetic acid reacted. All of these measurements were again performed using 0.04 Bar of acetic acid and 0.08 Bar of propene, with a total flow rate of 50 ml/min. Fig. 2(a) indicates that there is no reaction at 425 K; prob; significant product formation began at temperatures above 450 K. As shown in Fig. 2(b), the acetate selectivity drops steadily in the temperature range from 450 to 525 K, with the ketones formed by dehydration of the acetate products making up most of the difference. Above 525 K, secondary reaction pathways begin to dominate. The products formed at 600 K contain acetone (30% selectivity) and higher molecular weight hydrocarbons (20% selectivity).

In Fig. 3, we plot the effect of changing the composition of the reactants at 450 K on the products that are produced. For these experiments, the conversion of acetic acid was maintained between 10 and 12%, but the partial pressure of acetic acid was allowed to vary between 0.066 and 0.04 Bar, while the propene partial pressure varied between 0.066 and 0.16 Bar. At a propene:acetic acid reactant mole ratio of 1, a major product was acetone, which is formed when acetic acid is allowed to react with itself. When the mole ratio of reactants is increased to 2, acetone formation is completely suppressed and the selectivity to the propyl acetates is very high. This selectivity remains almost constant with further increases in the propene:acetic acid mole ratios. It is noteworthy that there is almost no production of the hydrocarbon products one would associate with the reaction of propene

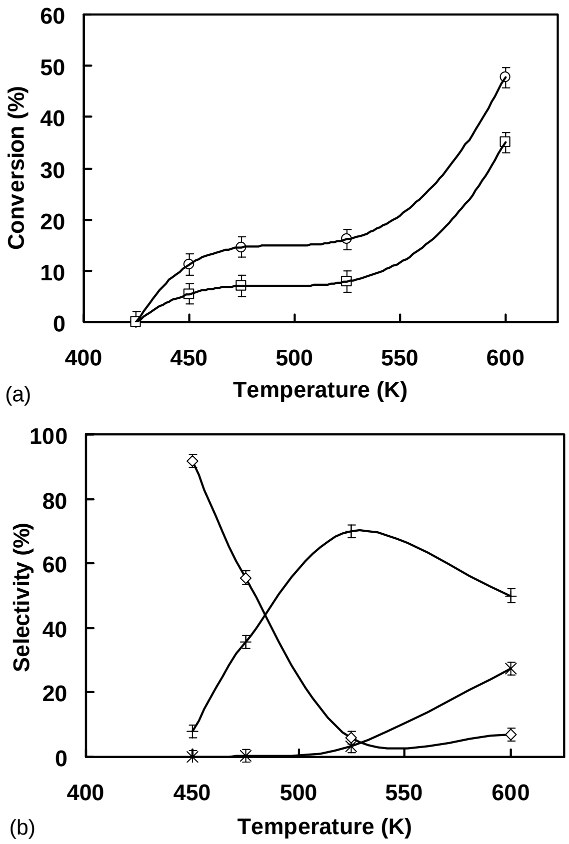

Fig. 2. Effect of reaction temperature on the conversion of the reactants and on the selectivity for acetic acid over the H-[Fe]ZSM-5 sample. For these experiments, the propene partial pressure was 0.08 Bar and the acetic acid partial pressure was 0.04 Bar. (a) Conversion of acetic acid (○) and propene (☐); (b) Selectivity to isopropyl acetate (◇), 3 methyl, 3-butene-2-one (+), and $\geq C_7$ hydrocarbons (×).

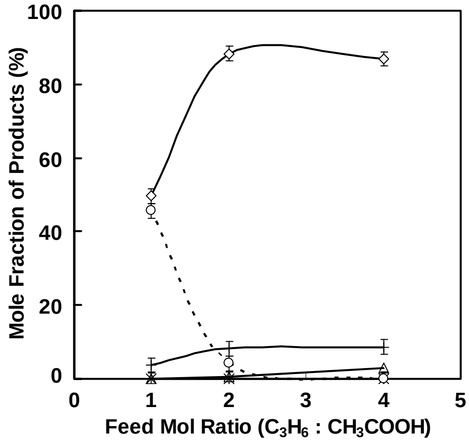

Fig. 3. The product distribution at 450 K over H-[Fe]ZSM-5 with different propene:acetic acid mole ratios. The products were isopropyl acetate (◇), acetone (○), 3-methyl-3-butene-2-one (+), isobutene (△), and $\geq C_7$ hydrocarbons (×).

at this temperature, even at the highest propene:acetic acid ratio.

Finally, Fig. 4 shows the typical time-on-stream behavior of the H-[Fe]ZSM-5 sample during alkylation at 475 K, at a total flow rate of 50 ml/min, with propene and acetic acid partial pressures of 0.08 and 0.04 Bar. The results show an initial transient during the first two hours. This transient behavior is most likely related to the formation of products inside the cavity. As the reactions progress, these products may affect the acid site by imposing spatial constraints that will ultimately affect the final product selectivities. After this transient, the catalytic performance was completely stable for the duration of this test. Indeed, during the course of several weeks of catalytic testing, we did not find it necessary to regenerate the catalyst.

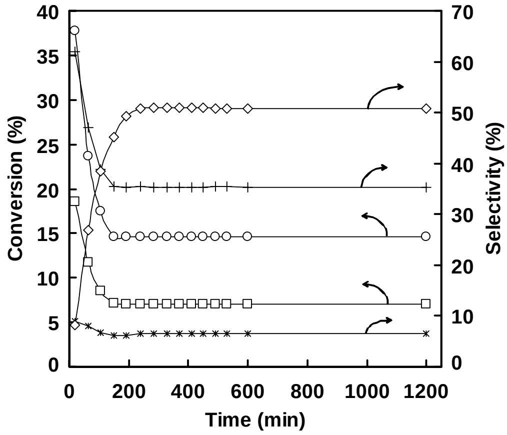

Fig. 4. Time on stream behavior observed for H-[Fe]ZSM-5 at 475 K using a propene partial pressure of 0.08 Bar and an acetic acid partial pressure of 0.04 Bar. The products were acetic acid (○), propene (□), isopropyl acetate (◇), *n*-propyl acetate (✱), and 3-methyl, 3-butene-2-one (+).

4. Discussion

The high selectivity and stability observed for the acylation of propene by acetic acid over these zeolite catalysts was surprising to us. In general, reactions involving propene on H-[Al]ZSM-5 are not stable in the temperature range between 450 and 550 K. Propene oligomerizes rapidly on this zeolite, even at room temperature [23–25]. While these oligomers can undergo cracking back to small olefins at about 450 K [23,25], hydride-transfer reactions also occur in this temperature range, leading to stable forms of hydrocarbons that block the zeolite pores and are difficult to remove [23]. From adsorption studies, acetic acid also decomposes over H-[Al]ZSM-5 above 450 K, forming very stable hydrocarbon deposits, possibly through oligomerization of intermediate acetone [33–37]. Again, these deposits would be expected to deactivate the catalyst with time on stream.

We believe that the high selectivity and stability exhibited by H-[Al]ZSM-5 for the acylation of propene is due to a fortunate interaction between the reactants at the acid sites. Acetic acid adsorbs very strongly on the acid sites in the zeolite, exhibiting a differential heat of adsorption of 140 kJ/mol for coverages below one molecule per site [39]. For temperatures below 550 K, this strong interaction will cause the acid sites to be essentially saturated with acetic acid and based on our previous study [32], the formation of the acetate intermediate from acetic acid will be slow at these temperatures. The experimental evidence that propene is excluded from the acid sites is that products that would normally be expected from the oligomerization of propene are not observed, even in a large excess of propene. With acetic acid, coking appears to occur through oligomerization of acetone that forms through an acetate intermediate [32]. Based on temperature-programmed-desorption (TPD) data, the acetate decomposes to CO_2 and a methyl group, which in turn is scavenged by a neighboring acetate group to form acetone. In the presence of excess propene, it appears that the acetate intermediate reacts with the olefin before it can decompose.

It is also interesting that H-[Al]ZSM-5 and H-[Fe]ZSM-5 exhibit similar catalytic activities, given that the acid sites associated with framework Fe are less reactive for reactions involving carbenium ions [23,40]. (Indeed, the difference in the consumption ratios for acetic acid and propene at 525 K may indicate that the stronger acid sites in H-[Al]ZSM-5 are responsible for secondary chemistry at this temperature). Based on calorimetric measurements with ammonia, pyridine [23,40], and acetonitrile [41], the stabilities of stable adsorption complexes in H-[Fe]ZSM-5 are similar to those in H-[Al]ZSM-5, so that the primary differences in catalytic activity appear to be due to differences in the stability of intermediate, carbocations. In the acylation of propene, the rate-limiting step likely involves decomposition of the adsorbed acetic acid to form the acetate intermediate. If this is true, then the barrier for forming the acetate intermediate would have to be similar for both solid acids.

Obviously, this conclusion must remain tentative at this time.

H-[Fe]ZSM-5 has not received much attention in the catalytic community, in part because of the view that it will not be stable under reaction conditions. While it is certainly true that special procedures, milder than that employed with H-[Al]ZSM-5, must be used for calcination of H-[Fe]ZSM-5, we found that H-[Fe]ZSM-5 was quite stable under the reaction conditions used in this study. H-[Fe]ZSM-5 seems to exhibit only minor advantages for the acylation of propene; however, previous work has shown that the hydride-transfer reactions which lead to coke formation are significantly suppressed on this material compared to H-[Al]ZSM-5 [23,40]. We suggest that H-[Fe]ZSM-5 should be considered more often for reactions where selectivity issues are important. Because Al impurities can dominate the chemistry of H-[Fe]ZSM-5 [40], care must be used in the synthesis of this material.

Finally, we believe the present work demonstrates the importance of adsorption studies for understanding reaction chemistry. While we do not claim that the adsorption studies we carried out with propene [23–25] and acetic acid [32] allowed us to predict reaction properties, they certainly guided us in choosing the temperature range in which reaction occurred and in explaining the chemistry that was observed. The approach of performing TPD and spectroscopic measurements on reactant molecules provides a simple method of screening and is particularly useful for understanding how these materials can be used in fine-chemicals synthesis.

5. Conclusions

The vapor-phase reaction between acetic acid and propene over acidic molecular sieves shows surprisingly high stability and selectivity. The saturation of the acid sites by acetic acid appears to control the available reaction pathways, preventing reactions that would lead to coke formation and stabilizing the product selectivity.

Acknowledgements

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