JOURNAL OF CATALYSIS **129**, 438–446 (1991)

Formation of Ketenes by Reaction of Carboxylic Acids over Alkali Metal-Exchanged Zeolites

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Received April 19, 1990; revised January 24, 1991

The formation of ketene from acetic acid by reaction over alkali metal-exchanged zeolites at ~350°C and low partial pressure is reported. Acetone and carbon dioxide are also produced. The greatest proportion of ketene was produced by the large-pore, faujasite zeolites exchanged with the smallest cations (Li^+ and Na^+). The corresponding ketenes from propanoic acid and isobutanoic acid, but not *n*-butanoic acid, were also observed. It was possible to react the ketene *in situ* by addition of a further reactant to the acetic acid feed, provided the additional reactant did not react with the zeolite catalyst. For example, methanol and dimethylamine were readily acetylated but ethanol reacted to produce ethene and water. Reaction of acetic acid with dimethylamine over NaY at 300°C gave a 70% conversion of dimethylamine with 100% selectivity to dimethylacetamide.

INTRODUCTION

Ketene (ethenone) is produced industrially from pyrolysis of acetic acid at 700 to 800°C under reduced pressure (0.1 to 0.5 atm), with an organic phosphate acting as an acid catalyst (*1*). The best conversion gives about 55 mol% ketene with a selectivity of 90 to 95% (*1*) with methane, carbon monoxide, carbon dioxide, and ethene as by-products. Slight changes in contact time shift these values appreciably, and a plant is only economic if it is run on a relatively large scale.

For production of higher ketenes, the direct pyrolysis of the carboxylic acid to its corresponding ketene is less efficient and cracking of the corresponding carboxylic anhydrides is a preferred synthetic route (*2*).

The reaction of acetic acid over acid zeolites has previously been studied in detail (*3, 4*) with the major products being acetone, carbon dioxide, and a mixture of hydrocarbons. No ketene was observed. However, no studies of the reaction of carboxylic acids over alkali zeolites have been reported. Herein, we report the products from the reaction of acetic acid at low partial pressure over alkali metal-exchanged zeolites and demonstrate that ketene is produced. Preliminary investigations into the scope of this reaction for ketene production, and the reactions of higher carboxylic acids are described.

METHODS

Thermal desorption mass spectrometry (td/ms (*5*)) was used to study the products evolved during the heating of a catalyst sample with sorbed reactant. Approximately 10 mg of the sample was placed in a silica tube and heated at 10°C min^{-1}. A constant flow of Ar carrier gas (12 ml min^{-1}) from a fixed glass capillary swept the evolved gas from the sample past the mass spectrometer inlet. The carrier gas was pumped by a vacuum pump resulting in a pressure of ~10 Torr over the sample. The mass spectrum of the carrier gas plus evolved gas was continuously scanned and recorded together with the temperature. This allowed any mass to charge ratio (*m*/*z*), within the mass range

0021-9517/91 $3.00

scanned, to be plotted versus sample temperature. The mass spectrum at a nominated temperature could also be obtained. Ion signals at m/z 40, 20, and 39 were not measured due to the presence of large peaks from the argon carrier gas. Detailed information on the equipment and software is given elsewhere (*5*).

Ketene was identified by mass spectrometry. Peaks at 42, 14, 41, 28, and 13 with relative intensities of 100, 82, 22, 8, and 4, respectively, compare well with published mass spectra (*6, 7*). The infrared spectrum of the gas phase product showed a strong band at 2150 cm^{-1} characteristic of the ketene C=O stretch (*8*). In principle, separation of ketene (or the dimer) followed by an accurate mass number determination is required for absolute identification. However, the simplicity of the starting reagent (acetic acid) and the observation of a clean, characteristic ketene mass spectrum make the assignment unambiguous. Comparison with published mass spectra (*6*) similarly identified methylketene (m/z 27, 28, 26, 56, 29, and 57 with relative intensities of 100, 47, 39, 31, 27, and 6) and dimethylketene (m/z 41, 42, 27, 43, 28, 70, 37 with relative intensities of 100, 39, 33, 29, 23, 15, and 9). A tentative identification was made for ethylketene as only the strongest two peaks in its mass spectrum (*6*) were observed (m/z 55 and 70 at relative intensities of 100 and 62).

In the figures, the ion signals have been scaled by sensitivity factors to give approximate mole ratios of the compound they represent. The ion signal for ketene at m/z 42 is plotted with ion signal contributions from the mass spectra of acetic acid and acetone subtracted. Most of the sensitivity factors have been determined experimentally from quantitative gas mixtures with Ar. A few of the sensitivity factors have been estimated from those of similar compounds and are considered to be correct within an order of magnitude. The figure captions state where estimated sensitivity factors have been used.

The same apparatus was also used as a mini-reactor at atmospheric pressure. The catalyst (~50 mg) was placed in a heated silica tube so that the carrier gas flowed through the sample, past the mass spectrometer inlet, and was vented to atmosphere. Reactants were introduced into the carrier gas by passing a portion of the carrier gas over the surface of the liquid reactant in an impinger. The flow rate of reactant through the sample was controlled by varying the temperature of the impinger and the ratio of reagent containing gas to the total carrier gas flow. For the acetylation experiments, using methanol and ethanol, a small amount of the alcohol was added to the acetic acid in the impinger.

Larger scale reactions were carried out over ~1 g NaY zeolite held in the centre of a 10-mm-diameter Pyrex tube by plugs of glass wool. Reagents were added by syringe pumps at 0.1 ml min^{-1} for acetic acid and a corresponding rate for the second reactant to give equimolar amounts, into a 1 ml s^{-1} nitrogen flow passing through the bed of zeolite maintained at 360°C. The effluent gas stream was cooled in a condenser, and the gas was then passed through a trap in an ice bath in order to collect liquid products. Products from the semi-preparative reactions were identified by gc/ms (gas chromatography mass spectrometry), by boiling point of the pure product and against an authentic sample using gas chromatography.

The NaZSM-5 sample was synthesized following a patented method (*9*) and contained 1.5 wt% Al. Zeolite Y was obtained from Union Carbide (Linde Y, SK40 lot No. 9680801014) and contained 8.5 wt% Al. Ion exchange of the sodium form was carried out by treating twice with fresh 1 *M* solutions of the appropriate chloride salt, then washing with distilled water. A range of zeolites and amorphous aluminosilicates were partially exchanged in this manner with Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Zn^{2+}, and La^{3+} cations. The Li^+-exchanged Zeolite Y contained 3.0% Na^+ (*10*).

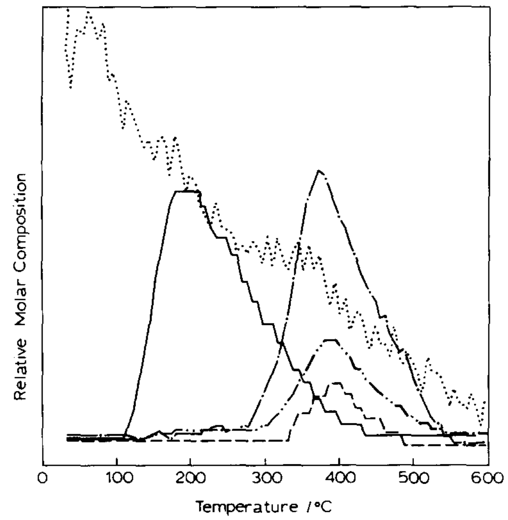


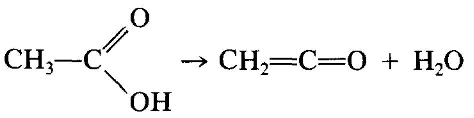
FIG. 1. Results from td/ms of acetic acid sorbed on NaZSM-5 at 150°C. The ion signal *m/z* 60 (——) represents acetic acid; *m/z* 42 (–·–) represents ketene; *m/z* 17 (····) represents water; *m/z* 44 (–··–) represents carbon dioxide; and *m/z* 58 (---) represents acetone.

RESULTS AND DISCUSSION

Reaction of Acetic Acid

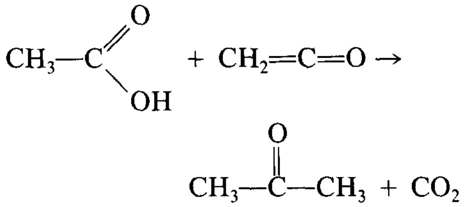
Ketene was observed by mass spectrometry during a study of the thermal desorption of acetic acid from alkali metal-cation-exchanged zeolites. The low pressure experimental conditions favoured the observation of ketene, as ketene would have reacted further under most experimental conditions.

The results from the low pressure thermal desorption of acetic acid from NaZSM-5, showing the initial observation of ketene, are given in Fig. 1. Physisorbed acetic acid desorbed from 150 to 440°C. Ketene reached a maximum of 370°C, and carbon dioxide and acetone peaked at 390°C. Ketene is formed from the decomposition of acetic acid to ketene and water:


(1)

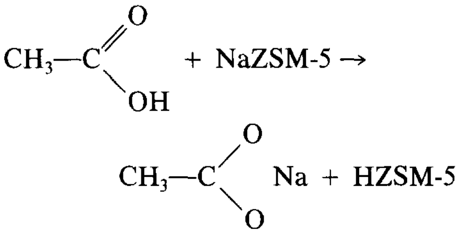
No significant water desorption peak was observed which coincided with the evolution of ketene. It is probable that the water desorption peak was spread over a large temperature range and difficult to observe above the background.

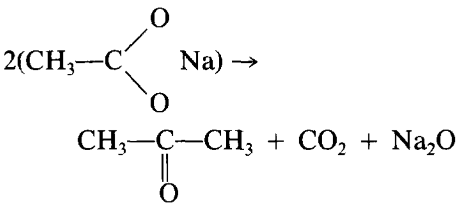
The coincidence of acetone and carbon dioxide and their evolution at a temperature higher than that of ketene, suggested that further reaction of acetic acid with ketene may have occurred to give acetone and carbon dioxide:


(2)

Ketene and acetic acid react to give acetic anhydride (*2*). However, no significant acetic anhydride was observed under these experimental conditions.

Alternatively, the formation of acetone and carbon dioxide could arise from reaction of acetic acid with the sodium cation to form the acetate. This would be followed by reaction of two molecules of sodium acetate to acetone and carbon dioxide:


(3)


(4)

$$2\text{HZSM-5} + Na_2O \rightarrow 2\text{NaZSM-5} + H_2O \quad (5)$$

The reaction products of acetic acid over

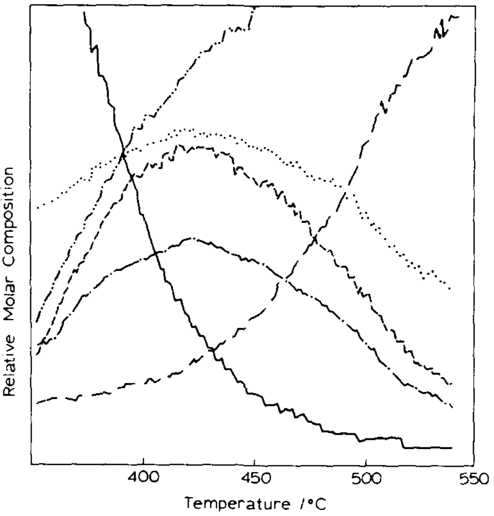


FIG. 2. Reaction products of acetic acid over NaZSM-5 versus temperature. (——) acetic acid (*m/z* 60); (—-—) ketene (*m/z* 42); (·····) water (*m/z* 17); (—··—) carbon dioxide (*m/z* 44); (---) acetone (*m/z* 58); and (– –) methane (*m/z* 16).

NaZSM-5 in a mini-reactor are shown in Fig. 2. The acetic acid flow was constant (0.5 h^{-1}) and the reactor temperature was increased at 2°C min^{-1} from 350°C. Unreacted acetic acid decreased as the reaction products ketene, acetone, and carbon dioxide increased. Ketene and acetone reached maxima at 420°C, then decreased as decomposition of acetic acid to methane and carbon dioxide became dominant at higher temperature. At all temperatures more acetone and carbon dioxide were produced than ketene. The simultaneous production of ketene, acetone, and carbon dioxide shows that the acetone and carbon dioxide were not reaction products of the ketene/acetic acid reaction.

A range of possible catalysts for ketene production were surveyed. These included amorphous aluminosilicates and zeolites exchanged with a range of cations. The products of thermal desorption of acetic acid from each sample were observed by mass spectrometry giving a rapid, although qualitative, test for ketene production. All the materials produced ketene to differing degrees, with the most effective catalysts being the largest-pore zeolites (faujasites) exchanged with the smallest cations (Li^+ and Na^+). As the cation size (and its basicity) increased, the temperature at which acetone and carbon dioxide were evolved decreased. The temperature of ketene desorption remained approximately constant. As a result, the amount of ketene observed decreased. This suggests that the reaction to acetone and carbon dioxide is base catalysed, and that the reaction to ketene is not. Ketene may result from reaction of acetic acid sorbed at sites other than the cation sites, such as structure defects.

Further experimental work was carried out using Li^+- and Na^+-exchanged Zeolite Y and NaZSM-5. The reaction products of acetic acid over one of the more effective catalysts, NaY, are shown in Fig. 3. Conditions similar to those for NaZSM-5 were used (Fig. 2) so a comparison can be made. For NaY, up to 460°C, more ketene was produced than acetone or CO_2. Under these conditions the yield from acetic acid at 400°C was 21%, with a product selectivity of

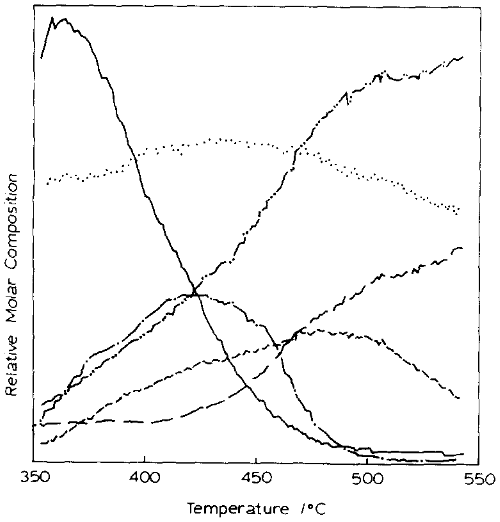


FIG. 3. Reaction products of acetic acid over NaY versus temperature. (——) acetic acid (*m/z* 60); (—-—) ketene (*m/z* 42); (·····) water (*m/z* 17); (—··—) carbon dioxide (*m/z* 44); (---) acetone (*m/z* 58); and (– –) methane (*m/z* 16).

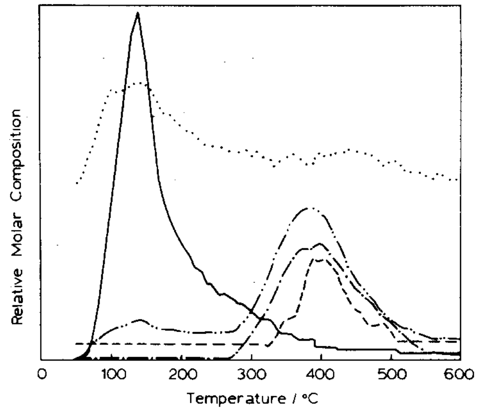
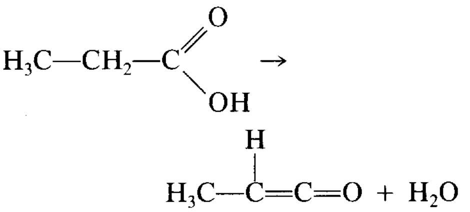


FIG. 4. Results from td/ms of propanoic acid sorbed on NaZSM-5 at 21°C. The ion signals have been scaled by estimated sensitivity factors to give approximate mole ratios. (——) propanoic acid (*m/z* 74); (–·–) methylketene (*m/z* 56); (·····) water (*m/z* 17); (---) pentane-3-one (*m/z* 86); (–··–) carbon dioxide (*m/z* 44).

38%. After holding the catalyst temperature constant at 400°C for 4.5 h the catalyst became black but 19% conversion to ketene was still observed. However, the low conversion and selectivity to ketene compared to thermal cracking means that reaction of acetic acid over zeolite catalysts is not an economic method for ketene production.

Reaction of Higher Carboxylic Acids

Higher carboxylic acids were investigated to determine whether a similar reaction to the corresponding ketene would occur. By analogy, propanoic acid would react to methylketene (propen-1-one) and water:



$$H_3C{-}CH_2{-}C(=O)OH \rightarrow H_3C{-}CH{=}C{=}O + H_2O \quad (6)$$

Pentan-3-one and carbon dioxide should also be observed as competing products.

The ion signals observed during td/ms of propanoic acid sorbed on NaZSM-5 at 21°C are shown in Fig. 4. Physisorbed propanoic acid (*m/z* 74) desorbed with a maximum at 140°C. Methylketene, shown by *m/z* 56, reached a maximum at 380°C. Pentan-3-one (*m/z* 86), identified by comparison with a published mass spectrum (*8*), and carbon dioxide showed maxima at ~400°C.

The td/ms results for isobutanoic acid sorbed on LiY at 21°C are shown in Fig. 5. Unreacted isobutanoic acid (*m/z* 73) desorbed first, reaching a maximum at 220°C. Dimethylketene desorbed with a maximum at 360°C and is shown here by the ion signal at *m/z* 41. No ketone (2,4-dimethylpentan-3-one) or carbon dioxide were detected. This may have been due to steric constraints within the zeolite. The only other major product observed had a strong ion signal at *m/z* 28 and was probably carbon monoxide. The correlation between ketene and carbon monoxide production (Fig. 5) suggests that the carbon monoxide results from decomposition of the ketene with further reaction to form coke.

The td/ms results of *n*-butanoic acid sorbed on LiY at 21°C are shown in Fig. 6. Physisorbed *n*-butanoic acid and water desorbed first. This was followed by a

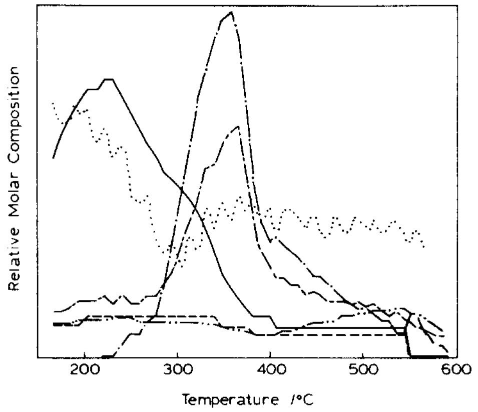


FIG. 5. Results from td/ms of isobutanoic acid sorbed on LiY at 21°C. The ion signals have been scaled by estimated sensitivity factors to give approximate mole ratios. (——) isobutanoic acid (*m/z* 73); (–·–) dimethylketene (*m/z* 41); (····) water (*m/z* 17); (---) 2,4-dimethylpentanone (*m/z* 71); (–··–) carbon dioxide (*m/z* 44); (–·–) CO (*m/z* 28).

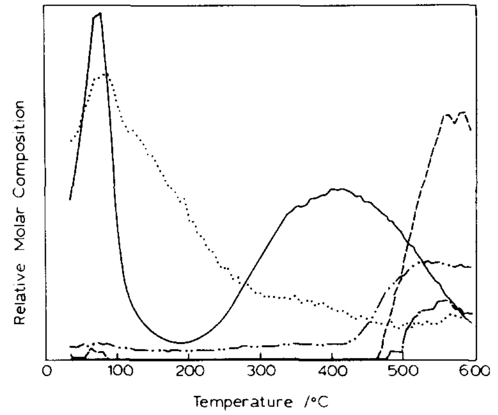
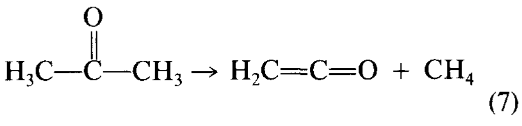


FIG. 6. Results from td/ms of *n*-butanoic acid sorbed on LiY at 21°C. The ion signals have been scaled by estimated sensitivity factors to approximate mole ratios. (——) *n*-butanoic acid (*m/z* 60); (–·–) ethylketene (*m/z* 70); (·····) water (*m/z* 17); (----) heptane-4-one (*m/z* 71); (–··–) carbon dioxide (*m/z* 44).

broad, higher-temperature signal (200 to 600°C) of more strongly bound *n*-butanoic acid. In contrast to the smaller carboxylic acids and isobutanoic acid, no reaction occurred until temperatures greater than 420°C were attained, when carbon dioxide and heptan-4-one appeared. There may also have been a small amount of ethylketene (*m/z* 70). An unambiguous identification was not possible from the mass spectra obtained. This shows a decreasing reactivity of the carboxylic acids with increasing chain length, as is also observed in the more conventional pyrolysis methods (*2*).

Reaction of Acetone

The possibility of a similar reaction occurring with acetone was investigated because ketene is also formed by pyrolysis of acetone at 700 to 800°C and atmospheric pressure (*1*):



$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 \rightarrow H_2C{=}C{=}O + CH_4 \qquad (7)$$

This reaction is less endothermic than that for acetic acid (*1*) and therefore ketene is formed more readily.

Reaction products from a constant flow of acetone over LiY in the mini-reactor with the temperature increasing at 5°C min^{-1} are shown in Fig. 7. The unreacted acetone concentration decreased with increasing temperature, but no major gaseous products were observed, with only a slight increase in methane above 500°C. The zeolite was black after the run, showing some coke formation.

In Situ Reactions

Ketene prepared over a zeolite catalyst could either be isolated from the process stream before further reaction, or reacted *in situ* by addition of a reactant to the carboxylic acid. The ketene would react rapidly, probably inside the catalyst. Advantages of this in situ reaction would be that reaction of acetic acid (ketene) and the second reactant to a product could be carried out as a single-step process and that shape-selective control over product distributions may occur. A major requirement should be that the second reactant should not itself react with the zeolite.

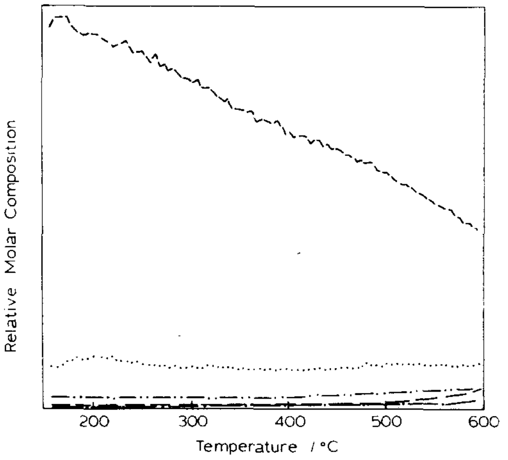


FIG. 7. Reaction products of acetone over LiY versus temperature. (---) acetone (*m/z* 58); (–·–) ketene (*m/z* 42); (····) water (*m/z* 17); (–··–) carbon dioxide (*m/z* 44); (– –) methane (*m/z* 16).

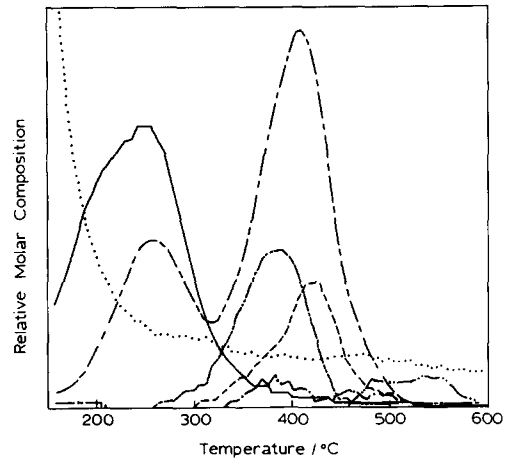
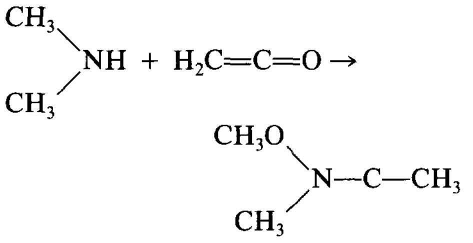


FIG. 8. Results from td/ms of dimethylamine and acetic acid sorbed on LiY at 21°C. (——) acetic acid (*m/z* 60); (–-–) ketene (*m/z* 42); (---) acetone (*m/z* 58); (–··–) carbon dioxide (*m/z* 44); (–––) dimethylamine (*m/z* 30); (––––) N,N-dimethylacetamide (*m/z* 87). Ion signals for dimethylamine and N,N-dimethylacetamide have been scaled by estimated sensitivity factors.

Acetylation of Dimethylamine

Acetylation of dimethylamine produces dimethylacetamide:



(8)

An initial td/ms experiment of a mixture of acetic acid and dimethylamine added to LiY showed the formation of dimethylacetamide (Fig. 8). Unreacted physisorbed acetic acid and dimethylamine desorbed first. From 260°C, with a maximum at 380°C, dimethylacetamide was observed followed by ketene, acetone, then carbon dioxide. More strongly bound dimethylamine also desorbed in this temperature range.

On a semi-preparative scale, a 60% aqueous dimethylamine solution was added to the acetic acid stream passing through the NaY catalyst bed at 360°C. A 70% conversion of dimethylamine with 100% selectivity to dimethylacetamide was obtained.

A recent patent for the preparation of dimethylacetamide uses an acid zeolite catalyst (*11*). Methanol and acetonitrile were reacted over HY to give a mixture of dimethylacetamide (40.8%) and methylacetamide (37.9%). The high selectivity of the reaction over the alkali metal-exchanged zeolites means that this reaction could be a useful method for production of dimethylacetamide.

Acetylation of Alcohols

Reaction of ketene with an alcohol gives the corresponding ester. Methanol and acetic acid were reacted together over LiY in the mini-reactor to determine whether this reaction would occur over an alkali metal-exchanged zeolite. The reaction products observed as the temperature increased are shown in Fig. 9. Methyl acetate was observed between 220 and 520°C, reaching a maximum at 320°C. Ketene appeared at a higher temperature than with acetic acid

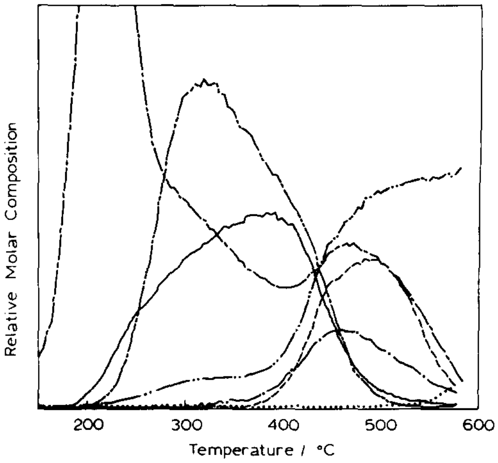


FIG. 9. Reaction products of methanol and acetic acid over LiY versus temperature. (–––) methanol (*m/z* 31); (–··–) methyl acetate (*m/z* 74); (——) acetic acid (*m/z* 60); (–-–) ketene (*m/z* 42); (----) acetone (*m/z* 58); (–·–) carbon dioxide (*m/z* 44); and (·····) hydrogen (*m/z* 2).

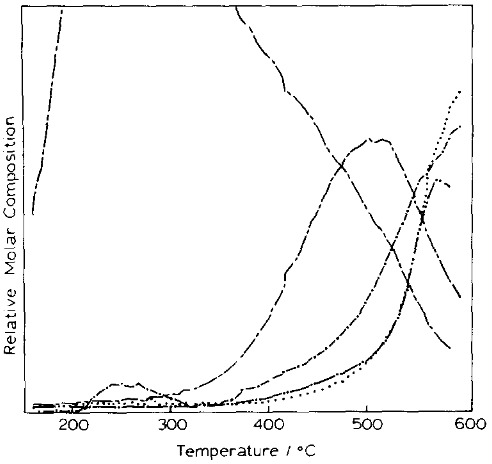


FIG. 10. Reaction products of methanol over LiY versus temperature. (–––) methanol (*m*/*z* 32); (–·–) dimethylether (*m*/*z* 46); (– –) formaldehyde (*m*/*z* 30); (–··–) carbon dioxide (*m*/*z* 44); and (·····) hydrogen (*m*/*z* 2).

alone as, at lower temperatures, it was probably being consumed by reaction with methanol. From 370°C, carbon dioxide rapidly increased, together with a small amount of acetone up to ~480°C. Above this temperature the amount of acetone reduced, possibly due to further reaction. From 540°C a small amount of hydrogen was also observed. When acetic acid was not present (Fig. 10) methanol reacted from ~300°C to form dimethylether (DME). Above 500°C the DME decreased with the formation of carbon dioxide, hydrogen and formaldehyde. DME and formaldehyde were not observed in the presence of acetic acid, showing the preferential reaction of methanol with acetic acid to methyl acetate.

Methylpropanoate was identified as the major product in an initial experiment in which methanol and propanoic acid was reacted over LiY at 360°C in the mini-reactor. On a semi-preparative scale, methyl propanoate was formed with a conversion of about 45% with no significant additional products.

The reaction products of ethanol and acetic acid over LiY are shown in Fig. 11. At temperatures below 200°C, mainly ethanol was observed, probably due to the acetic acid being sorbed onto the zeolite. At 260°C both ethyl product and acetic acid reached a maximum. Further ethyl acetate production at higher temperatures was limited by reaction of ethanol to ethene and water. From 350°C, carbon dioxide and acetone increased rapidly, followed by an increase in methane from 460°C.

Only a small amount of ethyl acetate was produced because ethanol reacts readily over LiY to produce ethene, water, and carbon dioxide, as shown in Fig. 12. This limits the usefulness of this *in situ* reaction.

The products from these experiments are those that would be predicted from acetylation of the second reactant by ketene. However, this is not proof that the reactions occur via ketene, as alternative mechanisms, such as dehydration reactions, are also possible. For example, acetic acid and methanol react over an acid catalyst to form methyl acetate and water.

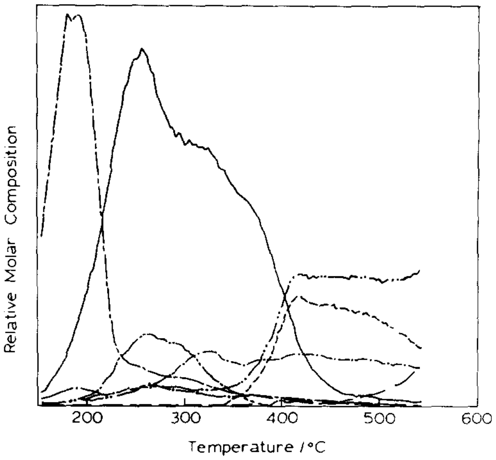


FIG. 11. Reaction products of ethanol and acetic acid over LiY. (–––) ethanol (*m*/*z* 31); (–··–) ethylacetate (*m*/*z* 61); (——) acetic acid (*m*/*z* 60); (–·–) ketene (*m*/*z* 42); (---) acetone (*m*/*z* 58); (–··–) carbon dioxide (*m*/*z* 44); (-·-·-) ethene (*m*/*z* 26); (– –) methane (*m*/*z* 16). The ion signal for ethylacetate has been scaled by an estimated sensitivity factor.

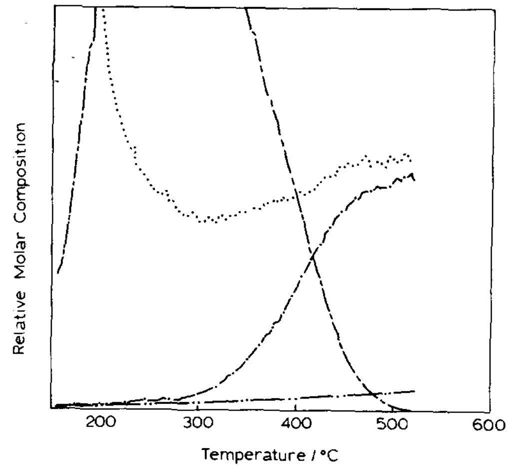


FIG. 12. Reaction products of ethanol over LiY versus temperature. (——) ethanol (*m/z* 31); (-···) ethene (*m/z* 26); (–·–) carbon dioxide (*m/z* 44); and (·····) water (*m/z* 17).

CONCLUSIONS

The conversion of acetic acid, propanoic acid, and isobutanoic acid to the corresponding ketene occurs as a general reaction over the alkali metal-exchanged zeolites investigated here. *n*-Butanoic acid showed low reactivity.

The expected products of the *in situ* acetylation reactions of ketene with alcohols and dimethylamine were observed. The reactions occurred readily with few side reactions provided the reactant itself did not react readily with the catalyst. For example, methanol and dimethylamine were readily acetylated, whereas ethanol reacted to ethene and water.

The low product selectivity means that commercial use of the reaction of carboxylic acids over alkali metal-exchanged zeolites to ketenes is probably not feasible. However, reactions over alkali metal-exchanged zeolites have interesting possibilities that should be explored further.

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