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Catalytic synthesis of butylketene and hexylketene from hexanoic acid and octanoic acid on functionalized silica monoliths at short contact times

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Abstract

Butylketene and hexylketene have been synthesized by catalytic dehydration of hexanoic and octanoic acids, respectively, over functionalized silica monoliths. The efficacy of silica for production of low molecular weight ketenes can be extended to higher molecular weight ketenes without any compromise in selectivity. For instance, the catalytic dehydration of octanoic acid was demonstrated to produce hexylketene with carbon selectivities on the order of 90% at temperatures between 745 and 795 K over a functionalized silica monolith. The results indicate that the control of contact time is a valid strategy for maximizing yield in catalytic ketene synthesis. Also, the ketene synthesis process can be integrated easily with ketene derivatization to prepare esters, in high yields.

Keywords: Ketenes; Butylketene; Hexylketene; Hexanoic acid; Octanoic acid; Silica monolith

1. Introduction

Ketenes with alkyl groups containing 10–20 carbons are produced from natural fatty acids by dehydrohalogenation of their corresponding acid chlorides with stoichiometric quantities of tertiary amines, like Et_3N, in an organic solvent [1]. These aldoketenes are very reactive and dimerize in situ to produce the lactone dimers which have been used as sizing agents for the paper industry. This technology is a non-catalytic, multiple step process involving toxic and corrosive reactants, solvents and by-products which must be disposed adequately. The direct synthesis of higher molecular weight ketenes by catalytic dehydration of carboxylic acids on silica monoliths could represent a more benign and environmentally safer alternative to the dehydrohalogenation technology.

Martinez et al. [2,3] reported that ketene and dimethylketene can be synthesized by dehydration of acetic acid and isobutyric acid, respectively, over functionalized silica monoliths. Molar yields of ketene and dimethylketene of more than 80% per pass were routinely achieved. These results and the fact that the catalytic production of C_2–C_5 ketenes showed no significant dependence on carbon number [4,5] make technically feasible the production of higher molecular weight ketenes by catalytic dehydration of the corresponding carboxylic acid over functionalized silica monoliths.

However, there are some experimental barriers to the catalytic dehydration of higher molecular weight carboxylic acids. The first is the low vapor pressure of fatty carboxylic acids [6]. As the carbon number increases, the vapor pressure of the straight-chain carboxylic acids decays exponentially. Therefore, it is more difficult to introduce the acid into the monolith reactor by the method used for acetic and isobutyric acid experiments: passing the inert carrier gas through a bubbler containing the liquid carboxylic acid [3]. Therefore, hexanoic acid (caproic acid) and octanoic acid (caprylic acid) were chosen because they provide an adequate vapor pressure

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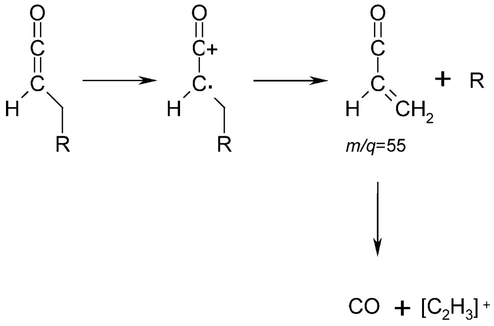
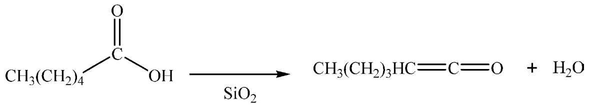
using the same experimental setup as for low molecular weight acids. However, a silicon oil bath was used instead of the water bath to reach higher bubbler temperatures and obtain higher values of the vapor pressure.

The second experimental problem is to find the adequate analytical technique to quantify the production of higher molecular weight ketenes in real time. The mass spectrometry (MS) has been reported to do so. However, the application of mass spectrometry as an analytical technique for the quantitative determination of the high molecular weight ketenes can be a difficult and challenging task. Of the ketene family, only the cracking patterns for ketene and dimethylketene have been recorded in the standard MS databases [7,8]. Because of the high reactivity of ketenes, few MS studies have been reported where the substrates themselves are introduced directly into the spectrometer [9,10]. Barteau and co-workers used MS for the catalytic dehydration of the carboxylic acids [4,5]. They used the signals for the parent mass of the ketenes and those at *m*/*q* values 1 and 28 mass units less to identify and quantify the C_2–C_5 ketenes. Maquestiau et al. [11] reported an extensive MS study of a series of alkylketenes synthesized by flash vacuum thermolysis of acid chlorides at 773–873 K. Some important conclusions can be drawn from that study. First, the cracking patterns of alkylketenes are very simple while those of carboxylic acids and carboxylic acid derivatives are rather complex. Second, the molecular ion peak for alkylketenes is, in general, very intense and this ion peak is the largest one for the case of ketene, methylketene, and ethylketene. For propylketene, butylketene, and pentylketene, the molecular ion peaks are still intense but the largest fragmentation is $m/q = 55$ for all of them. These results suggest that the main fragmentation pathway for alkylketenes is loss of an alkyl group by β-cleavage followed by loss of CO as depicted in the following scheme [11]:



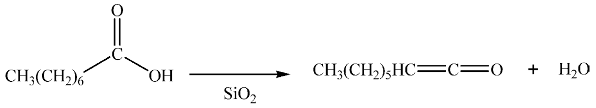
The authors also reported that when competitive β-cleavages are possible, the preferential elimination of the largest radical is observed. For the case of butylketene, Maquestiau et al. reported that the fragment, $m/q = 55$ is the most abundant, followed by the parental fragment, $m/q = 98$. Other detected fragments were $m/q = 27$, 42, 41, and 28. In our work, all these signals were monitored to track the formation of butylketene by catalytic dehydration of hexanoic acid on functionalized silica monoliths.



$$CH_3(CH_2)_4COOH \xrightarrow[SiO_2]{} CH_3(CH_2)_3HC{=}C{=}O + H_2O$$

Hexanoic acid Butylketene

Also, the cracking principles observed from C_2–C_7 alkylketenes by Maquestiau et al. may be used to predict the fragmentation pattern for the hexylketene expected as the product of octanoic acid dehydration.



$$CH_3(CH_2)_6COOH \xrightarrow[SiO_2]{} CH_3(CH_2)_5HC{=}C{=}O + H_2O$$

Octanoic acid Hexylketene

The fragment, $m/q = 55$, will be the principal hexylketene fragmentation channel. The signal for the parent mass at $m/q = 126$ must be present as well as signals from the β-cleavage and the CO loss, $m/q = 71$, 98, and 28. In this investigation, all of these signals were checked as fingerprints to track the formation of hexylketene by catalytic dehydration of octanoic acid on functionalized silica monoliths.

The goals of these experiments are to test the feasibility of the catalytic dehydration of heavier carboxylic acids (hexanoic acid and octanoic acid) to produce the corresponding alkylketenes using functionalized silica monoliths and to determine whether the short contact time approach is useful to promote higher alkylketene selectivity.

2. Experimental

2.1. Functionalized monolith preparation and characterization

The catalyst was prepared using the procedure patented by Martinez et al. [2]. Surface areas of plain and functionalized silica monoliths were measured by the BET method (Micromeritics 2010 ASAP). The samples were baked at 473 K overnight before measurements. While the surface area of the plain monolith was less than 2 m^2/g, the functionalized monolith had an enhanced surface area of 50 m^2/g. The morphology of the amorphous silica deposits was observed by optical microscopy (Nikon SMZ-2T).

2.2. Reactor setup

The reaction system has been described previously [3]. All the carboxylic acids (hexanoic acid 99.5%, Aldrich; octanoic acid 99.5%, Aldrich) were used as received. A hot silicone oil bath with a temperature controller was used to heat up the bubbler. The reactants, bubbler temperatures, and dosing conditions in the mass spectrometer are tabulated in Table 1.

A quadrupole mass spectrometer (MKS, Orion® Compact) with a differentially pumped UTI atmospheric pressure sampling module (APSM) was used to monitor product and

Table 1
Experimental conditions for the bubbler and dosing of the carboxylic acids

Carboxylic acid	Bubbler temperature (K)	Vapor pressure (Torr)	MS chamber pressure (Torr)
Hexanoic	373	10	9×10^{-7}
Octanoic	403	14	4×10^{-7}

feed compositions for the octanoic acid experiments. The APSM consisted of a zone enclosed by two gold plated orifice plates (a plate with 0.04572 mm orifice was used at the low-pressure side and a plate with a 0.07112 mm orifice was used at the high-pressure side) pumped to an intermediate pressure of around 10^{-2} Torr with a Welch Duo-Seal 1402 vacuum pump. The MKS mass spectrometer was controlled with Orion System Software Windows NT, Version 4.3.33. The MS probe was kept at approximately 403 K with an external heating mantle. The base pressure in the probe was about 4×10^{-8} Torr and increased to approximately 8×10^{-7} Torr during sampling. A Bayard-Alpert type ionization gauge tube driven by a Varian Model 843 vacuum ionization gauge controller measured the pressure at the mass spectrometer probe. An Edwards Diffstak Model 100-300M diffusion pump with Santovac 5® oil maintained the low pressure in the mass spectrometer probe and was backed by a roughing pump (Welch Model 1402).

For the hexanoic acid experiments, a different quadrupole mass spectrometer was used (SRS, PPR-300) with a stainless steel capillary (125 μm diameter and 0.9 m long) as a sampling probe. The capillary was kept at about 403 K with an electrical heating tape. A Varian turbomolecular pump (Model V70) maintained the low pressure in the mass spectrometer probe and was backed by a diaphragm pump (KNF). The PPR-300 mass spectrometer was controlled with a RGA Windows Software. The MS probe was also kept at approximately 403 K with an external heating mantle. The base pressure in the probe was about 5×10^{-8} Torr and increased to approximately 9×10^{-7} Torr during sampling.

2.3. Deconvolution

Deconvolution analysis of the overlapping mass spectrometer fragmentation patterns for the various reactants and products and the quantification of the products using sensitivity factors have been described previously [4,12]. A carbon balance was carried out by measuring the intensity decrease for the carboxylic acid during the reaction step and comparing it with the sum of the product signals.

2.4. Derivatization experiments

Since alkylketenes are more reactive than the corresponding carboxylic acids for the esterification of alcohols, qualitative confirmation of the production of alkylketene was provided by trapping the alkylketenes as the corresponding esters. The ketene stream from the continuous ketene production was bubbled into a glass tube (50 ml) containing approximately 20 ml of ethanol (absolute, Fisher) for 1–2 h. For the octanoic acid experiments, a sample from the glass tube was analyzed by gas chromatography (Hewlett-Packard, HP 5890) with a mass spectrometer detector (Hewlett-Packard, HP 5970B). A 25 m × 0.32 mm FFAP capillary column (AT-1000, Alltech) was used. For the hexanoic acid experiments, a sample from the glass tube was analyzed by GC (Hewlett-Packard, HP 6890) with a FID detector and using a 25 m × 0.32 mm FFAP capillary column (AT-1000, Alltech). The temperature programming for both GC analyses were: initial temperature = 313 K, initial time = 5 min, rate = 10 K/min, final temperature = 473 K, and final time = 5 min.

3. Results and discussion

Fig. 1 illustrates the MS output for the steady-state reaction of octanoic acid at 795 K with a He carrier flow of 250 sccm. The uncorrected mass spectrometer traces in Fig. 1 are divided into three regions to illustrate the experimental sequence. In the first region, helium bypassed the bubbler and reactor and the mass spectrometer background signals were determined for all fragments. In the second region, the reactant signal approached steady state after approximately 25 min. In the third region, the octanoic acid–helium flow was diverted to the monolith reactor. The signal for $m/q = 60$ was used to monitor the octanoic acid. As can be seen in the third trace of Fig. 1, the intensity of the octanoic acid signal ($m/q = 60$) drastically decreased upon

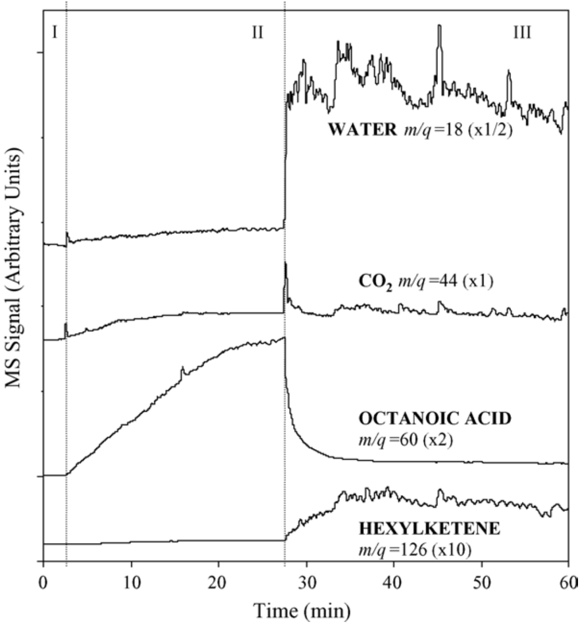


Fig. 1. Steady-state reaction of octanoic acid on functionalized silica monolith. Carrier flow rate = 250 sccm. Monolith temperature = 795 K. Region shows the MS signals for the background. Region II shows the MS of the reactant. Region III shows the MS of product stream. Partial pressure of octanoic acid = 14 Torr.

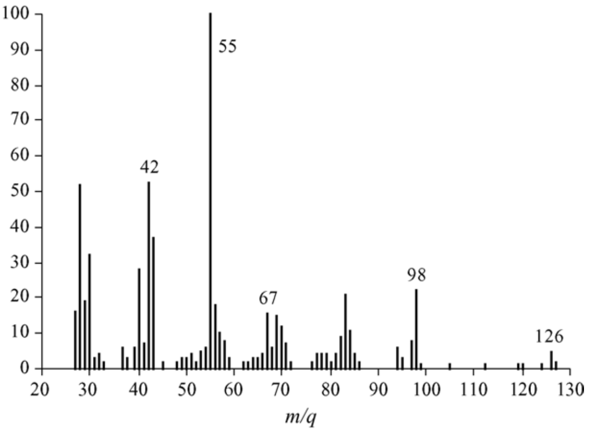


Fig. 2. Representative static MS cracking pattern in region III. Hexylketene production.

contact with the functionalized silica monolith. Simultaneously, there is a net increase in the signal for $m/q = 18$ (water), 44 (CO_2), and 126 (hexylketene). Other expected signals from hexylketene such as $m/q = 55$, 71, and 98 behaved in the same fashion as that for $m/q = 126$. Fig. 2 shows a representative static MS cracking pattern in the third region after subtraction of the acid, water, CO_2, and background contributions. It is evident that the signal for $m/q = 55$ is very intense. Therefore, the presence of $m/q = 55$, 71, 98, and 126 provides a clear fingerprint for the formation of hexylketene. No significant production of 8-pentadecanone, corresponding to the coupling of a pair of octanoates, was detected by monitoring signals for $m/q = 57$, 127, and 226. Although $m/q = 71$ is also a strong cracking fragment for the ketone and it increased when the reactant flow was directed to the reactor, it could not be used to monitor the ketone production because this fragment also corresponds to the hexylketene. Steady-state experiments with octanoic acid could not be carried out for more than 2 h because of the recurrent plugging of the orifice plates in the atmospheric pressure sampling module. During these short experiments, the extent of carbon deposition on the monolith was negligible. Therefore, the same monolith was used for all these experiments without attempting any regeneration procedure.

Fig. 3 shows the MS output for the reaction of hexanoic acid on a functionalized silica monolith at 805 K and a He flow of 300 sccm. Similar results to the octanoic acid experiments were obtained. In region III, there was a decrease of the hexanoic acid signal ($m/q = 60$) and increase in the water ($m/q = 18$), CO_2 ($m/q = 44$), and butylketene ($m/q = 55$ and 98). Fig. 4 shows a static MS cracking pattern after substraction of the acid signals, CO_2, water, and background contributions. Table 2 compares the mass spectra abundance obtained in this work with previous studies of Maquestiau et al. [11]. The presence of the signals $m/q = 28$, 42, 55, 70, and 98 and their relative abundance show clearly the butylketene production by catalytic dehydration of hexanoic acid over silica monoliths. As observed with the octanoic acid, there was no significant production of 6-undecanone which could be formed by coupling of a pair of hexanoates. In this case, the monitored signals were $m/q = 99$ and 170.

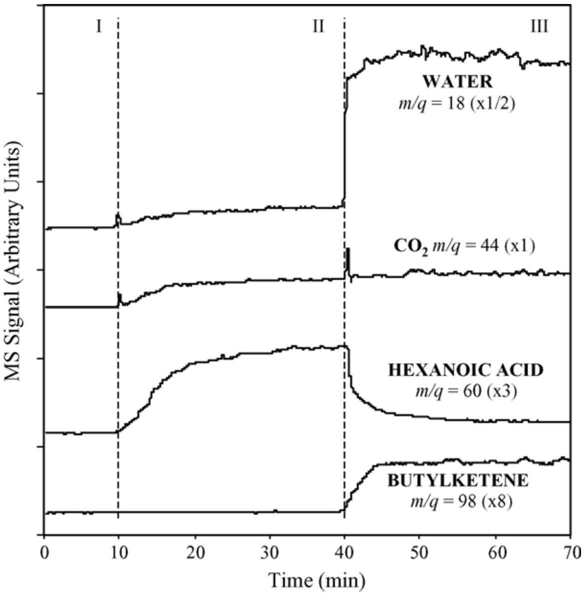


Fig. 3. Steady-state reaction of hexanoic acid on functionalized silica monolith. Carrier flow rate = 300 sccm. Monolith temperature = 805 K. Region I shows the MS signals for the background. Region II shows the MS of the reactant. Region III shows the MS of product stream. Partial pressure of hexanoic acid = 14 Torr.

Quantitative analysis of the products required deconvolution of the overlapping MS fragments for the carboxylic acids and other products as well as the application of sensitivity factors. Signals for the carboxylic acid, water and CO_2 were readily identifiable and their contributions were subtracted from the observed product fragmentation pattern. Deconvolution of hydrocarbon products arising from the decarboxylation reaction is difficult because of the overlapping hydrocarbon fragments from the alkylketene. Thus, it was assumed that *n*-heptane and CO_2 are produced in

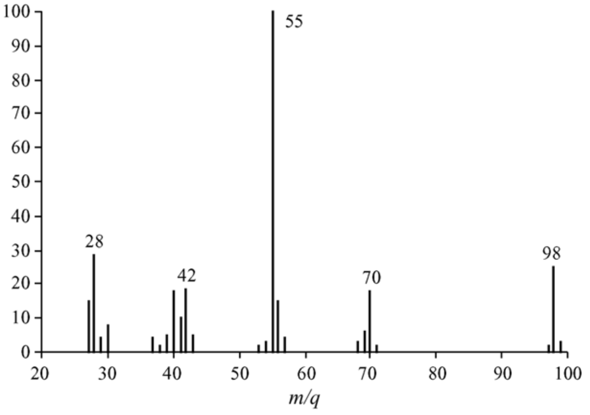


Fig. 4. Representative static MS cracking pattern in region III. Butylketene production.

Table 2
Comparison of mass spectra for butylketene

m/*q*	Maquestiau et al. [11]	This work
98	21	25
70	3	18
55	100	100
42	16	28
41	15	10
28	8	35
27	25	15

equal amounts for the octanoic acid experiments and *n*-pentane and CO_2 are produced in equal amounts for the hexanoic acid experiments and these hydrocarbon contributions were subtracted as well. The remaining fragmentation pattern was assigned to the corresponding alkyketene product. For the quantitative determination of hexylketene and butylketene yield, the signal $m/q = 55$ was chosen because of its intensity. Sensitivity factors were calculated according to Ko et al. [12]. A carbon balance was carried out by measuring the intensity decrease for the carboxylic acid due to reaction and comparing it with the sum of the product yields. The carbon balance was computed by multiplying the deconvoluted intensity for each product signal by the calculated sensitivity factors (1.0 for water, 1.4 for CO_2, 5.0 for octanoic acid at $m/q = 60$, 2.0 for hexylketene at $m/q = 55$, 4.6 for hexanoic acid at $m/q = 60$, and 1.8 for butylketene at $m/q = 55$) and the carbon number (the number of carbon atoms in the molecules). For the experiments shown in Fig. 2, the carbon content of the products was calculated to be 16% higher than the carbon provided by the octanoic acid. For the rest of the experiments, this deviation was always present and was of the order of 15–25%. This high deviation may reflect the uncertainty of the hydrocarbon deconvolution, the ‘‘assumed’’ cracking pattern for the hexylketene as well as the ‘‘noisy’’ signals from the mass spectrometer. For the hexanoic acid experiments, the carbon content of the products computed in this fashion was within 15% of the carbon provided by the reactant.

The contact time was varied adjusting the He carrier flow rate. Fig. 5 shows the variation of octanoic acid conversion and molar hexylketene selectivity (mol of hexylketene/mol of octanoic acid reacted) as a function of temperature and carrier flow rate. These results are similar to those reported previously for the acetic acid and isobutyric acid experiments by Martinez et al. [3]. The conversion increased monotonically but the hexylketene selectivity remained nearly constant when the monolith temperature was increased from 745 to 795 K. For example, at 795 K with a carrier flow of 250 sccm, the reactant conversion was 91.3% with a hexylketene selectivity of 91.8%. The contact time for this experiment is of the order of 500 ms. By increasing the helium flow rate from 125 to 250 sccm, the hexylketene selectivity is increased and the conversion-temperature profile shifted to higher temperatures. The important point is that the hexylketene selectivity is approximately 90% in the studied temperature range. Fig. 6 shows the results for the production of butylketene from hexanoic acid. These results are similar to those obtained for the octanoic acid experiments. The main result is that the high molar ketene selectivities observed for the acetic acid and isobutyric acid experiments are maintained for these higher molecular weight carboxylic acids.

After several hours of operation with the hexanoic acid, the functionalized monolith had darkened due to carbon deposition. The carbon was removed by heating the functionalized monolith in flow of air (250 sccm) at 700 K for 6 h. This resulted in a completely regenerated and carbon-free catalyst with the same activity as a fresh catalyst.

3.1. Ketene derivatization

Since alkylketenes are more reactive than the corresponding carboxylic acids for the esterification of alcohols, qualitative confirmation of the production of alkylketene was provided by independent derivatization experiment in which the gaseous stream exiting the monolith reactor was bubbled for 1–2 h into a glass tube containing approximately 20 ml of absolute ethanol. A blank derivatization experiment in which octanoic acid vapor was passed through an empty reactor at 750 K was also carried out. GC–MS analysis of these two experiments showed two main peaks. In the production of hexylketene experiment, a sharp and intense

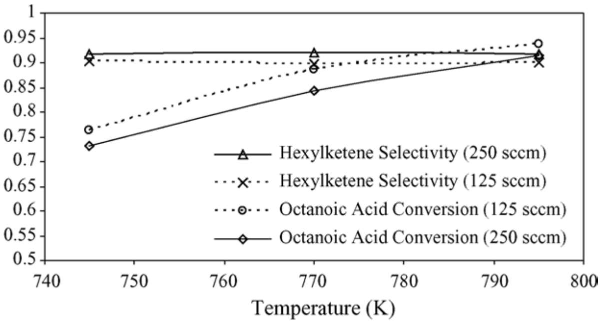


Fig. 5. Octanoic acid conversion and hexylketene selectivity as a function of helium flow rate and temperature.

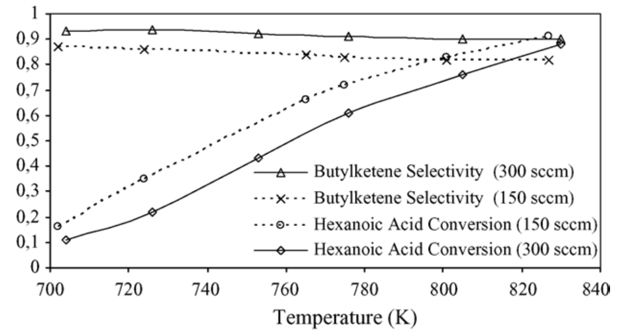


Fig. 6. Hexanoic acid conversion and butylketene selectivity as a function of helium flow rate and temperature.

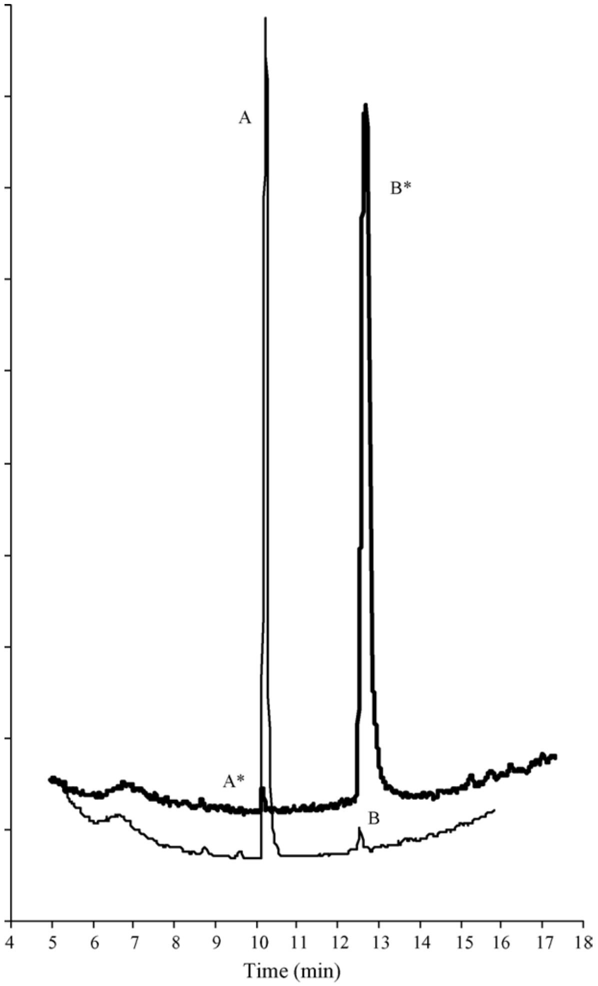


Fig. 7. GC of a sample from the reaction of hexylketene with ethanol (A and B). GC from a blank experiment (reaction of octanoic acid vapor with ethanol) (A^* and B^*).

peak (A) with a retention time of 10.29 min and a smaller peak (B) at 12.61 min were observed, as shown in Fig. 7. The uncorrected ratio of (A) peak area to (B) peak area was about 37.8. For the blank experiment, these two peaks were also observed: peak (A^*) with a retention time of 10.32 min and peak (B^*) with retention time of 12.64 min, respectively, as shown in Fig. 7. However, the ratio of (A^*) peak area to (B^*) peak area gave a completely different value, 0.0357. A MS scan analysis of (A) and (A^*) peaks showed that the compound eluted at this retention time is ethyl octanoate. A MS scan analysis of (B) and (B^*) peaks identified this compound as the octanoic acid. Similar results were obtained for the hexanoic acid experiments. In summary, these derivatization experiments show that the behavoir of the empty reactor is quite different from that of the functionalized silica monolith. For the empty reactor, the acid is not converted while for the functionalized silica monolith, the alkylketene is produced and it is immediately converted into the corresponding ester by reaction with ethanol.

4. Conclusions

In this study, the catalytic dehydration of octanoic acid was demonstrated to produce hexylketene, with carbon selectivities on the order of 90% at temperatures between 745 and 795 K over a functionalized silica monolith. The catalytic dehydration of hexanoic acid produces butylketene with molar selectivities on the orden of 90% at temperatures between 700 and 830 K. The presence of the alkylketenes was verified by on-line mass spectrometry and by trapping with ethanol to form the corresponding esters. These products were identified by independent GC–MS and GC experiments.

The symmetric ketones, 8-pentadecanone and 6-undecanone, the likely result of bimolecular coupling of octanoates and hexanoates, respectively, could not be detected in significant concentrations. However, its presence could not be ruled out due to their very low vapor pressures and low MS sensitivity.

In this study, contact time was varied by adjusting helium flow rate. It was observed that increasing the carrier flow rate (or decreasing the contact time) increases alkylketene selectivity. These results are similar to those for the production of ketene and dimethylketene from the corresponding carboxylic acids. Therefore, the most important result of this study is the demonstration that the efficacy of silica for production of low molecular weight ketenes can be extended to higher molecular weight ketenes without any compromise of selectivity. The use of short contact time improves the selectivity to the intermediate alkylketene.

Acknowledgments

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