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# Conversion of ethane to methanol and ethanol by ozone sensitized partial oxidation at near atmospheric pressure

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**Abstract**

The reaction of ethane–oxygen mixtures with ozone as a sensitizer in the feed-gas was quantitatively studied at near atmospheric pressure in a dual-flow system. Ozone was generated by silent discharge. The influence of reaction temperature, oxygen concentration in the feed-gas, residence time in the reactor, and ozone concentration in oxygen on the reaction were investigated.

Ethanol selectivities (based on carbon) between 3.95 and 21.8% and methanol selectivities between 17.1 and 41.0% with the combined formaldehyde–acetaldehyde–methanol–ethanol (FAME) selectivities between 36.7 and 95.7% were observed for ethane conversion equal to or less than 6.1%. The FAME selectivity was found to be over 90% when the ethane conversion was below 3.5%.

## 1. Introduction

The direct conversion of ethane to ethanol could be an inexpensive method for producing ethanol. Several such studies have been reported [1] and the kinetics and mechanism of ethane oxidation was studied [2,3]. Although the process of the direct conversion of ethane to ethanol is simple and energetically efficient, it still requires high temperature, since ethane is a very stable hydrocarbon, and high pressure, due to the thermodynamics and kinetics of the process.

Since the activation energy of the reaction of ethane with dioxygen is high [4],

$$C_2H_6 + O_2 \rightarrow CH_3CH_2 + HO_2 \quad E_a = 212.8 \text{ kJ/mol}$$

a catalyst or sensitizer is required to reduce the activation energy of the initiating reaction in order that the chain reactions that follows can proceed under milder reaction conditions. Unfortunately, most of the catalysts studied have led to greater over oxidation resulting in lower ethanol yield [5,6] and often no ethanol being detected.

We recently reported on the ozone sensitized partial oxidation of methane to methanal [1,7,8] and refer to the references therein for the early work.

## 2. Experimental

### 2.1. Apparatus

The reaction system, has been previously described [1a, 1c]. The ozone was generated by 15 kV to two Pyrex glass Berthelot ozonizer tubes in series and analyzed by the iodometric method. Pure $O_2$ gas was partially converted to ozone (5.5 mol%, 8.3 wt%) in the ozone generators. The gas mixture of $O_2$ and $O_3$ was thoroughly mixed with $C_2H_6$ in a glass bead mixing tube before passing into the reactor. The analysis of reactants and


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products was conducted by two on-line gas chromatographs as previously described.

### 2.2. Data processing

The conversions, yields and residence times were calculated as previously described [1a,1c,7]. Material balances for carbon, oxygen and hydrogen were calculated for each experiment. An average of the ratio of Mass(out) to Mass(in) and a standard deviation obtained for carbon, oxygen and hydrogen are as follows:

$$\frac{M_{Cout}}{M_{Cin}} = 0.990 \pm 0.009; \quad \frac{M_{Oout}}{M_{Oin}} = 1.094 \pm 0.088;$$

$$\frac{M_{Hout}}{M_{Hin}} = 0.993 \pm 0.007$$

## 3. Results and discussion

It was found that, without ozone in the feed-gas, no reaction was observed at reaction temperature of 282°C. However, with ozone in the feed, the major products were water, formaldehyde, acetaldehyde, methanol, ethanol and carbon dioxide. Methane, ethylene and carbon monoxide were also present in the products in almost all the experiments, except for the run at 252°C. Traces of formic acid and small amounts of butane were detected in the experiments carried out at higher temperatures. The results are given in Table 1.

### 3.1. Effects of reaction temperature

The change in the selectivities (based on carbon) of methanol, ethanol, formaldehyde, acetaldehyde, FAME, and carbon monoxide with reaction temperature is presented in Fig. 1. The selectivity of methanol obtained was higher than that of ethanol and reached its highest value at about 280°C. The selectivities of ethanol, formaldehyde, acetaldehyde and FAME increased as the reaction temperature was reduced. At reaction temperatures below 280°C the selectivity of FAME was over 90%. The variation trend of the selectivity of formaldehyde with reaction temperature was almost the same as that of acetaldehyde, indicating that the majority of formaldehyde was probably produced by the same precursors ($CH_3CH_2OO$ and $CH_3CH_2O$) as acetaldehyde. Since the selectivity of acetaldehyde is parallel to that of ethanol at higher reaction temperatures, it is probable that the majority of acetaldehyde and ethanol are produced via the same active species which might be $CH_3CH_2O$.

Table 1. Summary of the reaction conditions, the conversions of the reactants and the selectivities of the important products in the $O_3$ sensitized partial oxidation of ethane to ethanol. Reaction volume = 113.6mL. $[O_3]$ in $O_2$ ≃ 8(wt)% *$[O_3]$ = 0%
[a]RT=Residence time, [b]FAME=HCHO + $CH_3CHO$ + $CH_3OH$ + $C_2H_5OH$. E/M= Selectivity of ethanol / Selectivity of methanol

| Expt No. | Reaction condition | | | | Conversion | | Selectivity, Yield (based on carbon) | | | | | | E/M |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Temp (°C) | Press. (atm) | $O_2$ Concn in the feed (mol %) | RT[a] (min) | $C_2H_6$ | $O_2$ | CO | HCHO | $CH_3CHO$ | $CH_3OH$ | $C_2H_5OH$ | FAME[b] | |
| 59 | 352 | 1.45 | 5.70 | 5.49 | 6.06 | 98.3 | 35.3, 2.14 | 10.9, 0.663 | 5.29, 0.321 | 20.2, 1.22 | 4.31, 0.261 | 40.7, 2.47 | 0.213 |
| 60 | 370 | 1.45 | 5.24 | 5.47 | 5.87 | 100 | 35.4, 2.08 | 9.16, 0.538 | 6.49, 0.381 | 17.1, 1.01 | 3.95, 0.232 | 36.7, 2.16 | 0.231 |
| 65 | 281 | 1.45 | 5.84 | 6.82 | 3.60 | 58.2 | 3.53, 0.127 | 20.0, 0.719 | 14.1, 0.506 | 41.0, 1.48 | 14.2, 0.511 | 89.3, 3.22 | 0.346 |
| 66 | 252 | 1.35 | 6.59 | 6.06 | 0.869 | 18.3 | 0.00, 0.00 | 18.7, 0.163 | 26.6, 0.231 | 28.6, 0.249 | 21.8, 0.189 | 95.7, 0.832 | 0.761 |
| 67 | 281 | 1.45 | 9.89 | 6.58 | 4.68 | 53.6 | 18.0, 0.843 | 15.8, 0.741 | 9.90, 0.464 | 35.0, 1.64 | 13.9, 0.652 | 74.6, 3.50 | 0.398 |
| 68 | 281 | 1.45 | 14.0 | 6.23 | 5.82 | 44.5 | 16.7, 0.971 | 15.3, 0.889 | 13.4, 0.777 | 32.6, 1.90 | 14.1, 0.821 | 75.4, 4.39 | 0.433 |
| 69 | 281 | 1.55 | 14.6 | 4.24 | 4.24 | 32.6 | 4.66, 0.198 | 19.4, 0.823 | 15.6, 0.660 | 35.0, 1.48 | 16.8, 0.714 | 86.8, 3.68 | 0.481 |
| 70 | 281 | 1.35 | 11.5 | 9.52 | 5.26 | 51.6 | 24.9, 1.31 | 13.3, 0.698 | 12.5, 0.659 | 31.8, 1.67 | 10.7, 0.563 | 68.3, 3.59 | 0.337 |
| 71 | 300 | 1.45 | 5.71 | 6.14 | 5.33 | 97.7 | 29.2, 1.56 | 13.1, 0.698 | 8.52, 0.454 | 30.9, 1.65 | 7.13, 0.380 | 59.7, 3.18 | 0.230 |
| 72 | 267 | 1.40 | 5.52 | 6.24 | 1.58 | 32.7 | 5.04, 0.080 | 25.1, 0.398 | 21.5, 0.340 | 29.5, 0.467 | 14.7, 0.233 | 90.8, 1.44 | 0.499 |
| 63* | 282 | 1.35 | 6.6 | 6.06 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |

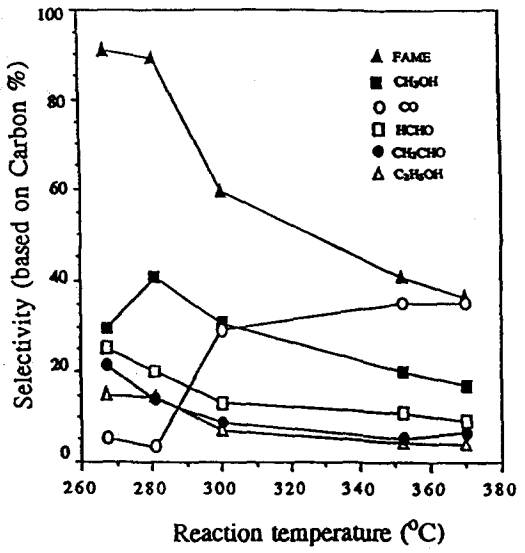


Fig. 1. Variation of selectivity with reaction temperature. Residence time: 5.47–6.82 min, reaction pressure: 1.40–1.45 atm, $O_3$ concentration in $O_2$: ca. 8 (wt)%, $O_2$ concentration in feed-gas: 5.24–5.71 (mol)%.

It is interesting to compare the trend of the selectivity of FAME with reaction temperature to that of carbon monoxide. The change of the selectivity of FAME with reaction temperature is almost inversely related to that of carbon monoxide, indicating that the reduction of selectivity of FAME with increase in reaction temperature was caused by FAME being further oxidized to carbon monoxide. It is clearly demonstrated in Fig. 1 that lower reaction temperature favours the formation of alcohol and the preservation of FAME.

### 3.2. *Effect of oxygen concentration in the feed-gas*

The influence of oxygen concentration in the feed-gas on the selectivity is presented in Fig. 2. The selectivity of ethanol was almost independent of the oxygen concentration. The selectivity of both methanol and formaldehyde diminished with increase in oxygen concentration in the feed-gas, but decreased more in the oxygen concentration range from 6 to 10% than in the range from 10 to 14%. The selectivity of FAME decreased as the oxygen concentration in the feed-gas was increased from 6 to 10% and, at oxygen concentration higher than 10%, the selectivity became almost independent of the oxygen concentration. The decrease of the selectivity of methanol and formaldehyde with increasing oxygen concentration was most probably attributable to the further oxidation of methanol and formaldehyde to carbon monoxide, demonstrated in Fig. 2 by the opposite trend of the selectivity of carbon monoxide with oxygen concentration to those of methanol and formaldehyde.

More oxygen was consumed than the $O_3$ present indicating that the $O_3$ initiated the reaction permitting the $O_2$ to react with and forming the intermediate chain carrying free radicals.

### 3.3. *Effect of residence time*

The influence of residence time on the ozone-sensitized ethane oxidation was investigated at the reaction temperature of 281°C, reaction pressures from 1.35–1.55 atm. and oxygen concentrations in the feed-gas between 11.5 and 14.6 (mol)% with ≈8 (wt)% ozone in oxygen in the feed-gas.

Fig. 3 shows the variation of selectivities of methanol, ethanol and FAME with change in residence time. All the selectivities decreased with

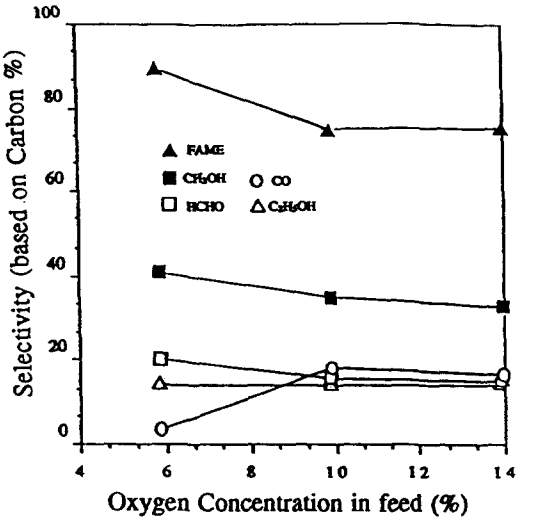


Fig. 2. Variation of selectivity with $O_2$ concentration in the feed. Residence time: 6.23–6.82 min, reaction pressure: 1.45 atm, [$O_3$] in $O_2$: ca. 8 (wt)%, reaction temperature: 281°C.

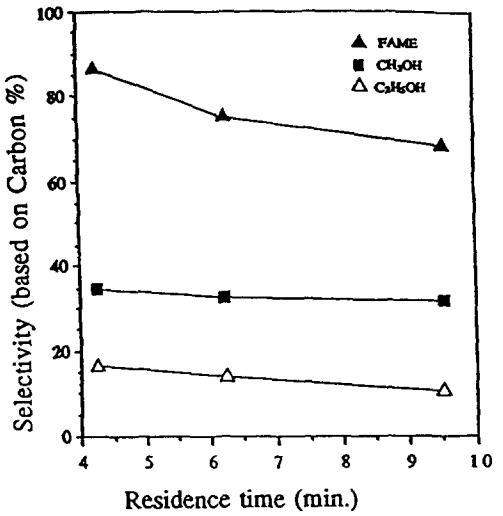


Fig. 3. Variation of selectivity with residence time. Reaction pressure: 1.35–1.55 atm, reaction temperature: 281°C, [$O_3$] in $O_2$: ca. 8 (wt)%, [$O_2$] in the feed: 11.5–14.6 (mol)%.

increase in the residence time. The highest selectivities were obtained at the lowest residence time. Further reduction of the residence time was limited by the back pressure from the sampling valves in the gas chromatographs.

### *3.4. Variation of the selectivities with the conversion of ethane*

Fig. 4 shows the changes in the selectivities of ethanol, methanol and FAME as a function of the conversion of ethane. The selectivities of both FAME and ethanol increased with the decrease in conversion of ethane. The selectivity of FAME increased very rapidly from ≈0% to 86% as the conversion of ethane was decreased from 7.1% to 4%. In the range of the conversion of ethane below 3%, further reducing the conversion of ethane caused only a slight increase in the selectivity of FAME. In order to obtain a high selectivity of FAME, the conversion of ethane should be controlled at below 4%. For ethanol, the selectivity increased slowly as the conversion of ethane was decreased from 6.4% to 4.6% and further decreasing the conversion from 4.6% to 2.0% only resulted in a very slight increase of the selectivity. At the conversion of ethane below 2%, the selectivity of ethanol increased more quickly with decrease in the conversion of ethane. The selectivity of methanol passed through its maximum value at the ethane conversion of ≈4%.

## 4. Reaction mechanism

Though no direct reaction was observed between $O_3$ and $C_2H_6$ at room temperature, it cannot be entirely ruled out to occur at higher temperatures. The first step is believed to be ozone decomposing to dioxygen and an oxygen atom

$$O_3 \rightarrow O_2 + O \quad (E_a = 92.80\ \text{kJ/mol}) \qquad (1)$$

followed by the oxygen atom reaction with ethane to generate an ethyl free radical.

$$O + C_2H_6 \rightarrow C_2H_5 + OH \quad (E_a = 32.84\ \text{kJ/mol}) \qquad (2)$$

The reaction is believed to proceed by the free radical chain reaction mechanism proposed [1a].

Methanol could be produced from $CH_3CH_2OO$ via the reaction sequence

$$CH_3CH_2OO \rightarrow CH_3O + HCHO \qquad (3)$$

and

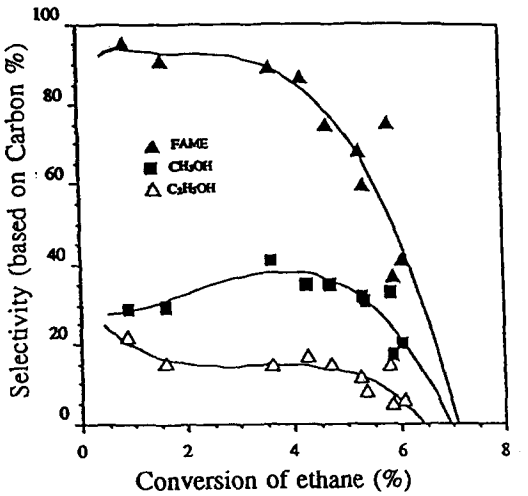


Fig. 4. Variation of selectivity as a function of conversion. Reaction pressure: 1.35–1.55 atm, reaction temperature: 252–370°C, residence time: 4.24–9.52 min, [$O_3$] in $O_2$: ca. 8 (wt)%, [$O_2$] in the feed: 5.24–14.6 (mol)%.

$$CH_3O + C_2H_6 \rightarrow CH_3OH + C_2H_5 \quad (4)$$

The ratio of the recombination to the disproportionation reaction of $C_2H_5$ radicals is independent of reaction temperature and since at lower temperature ethylene was detected but no butane was observed, this indicates that the ethylene formed at lower temperature was not produced by the disproportionation reaction, but by other reactions, for example,

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \quad (5)$$

and

$$C_2H_5O \rightarrow C_2H_4 + OH \quad (6)$$

## 5. Conclusions

Ozone can significantly sensitize the ethane–oxygen reaction and enhance the formation of methanol and ethanol at near 1 atm pressure. The reaction temperature, oxygen concentration in the feed, and residence time can significantly influence the conversions of the reactants and the selectivities of the products. The reaction temperature is the main parameter affecting the selectivities of the products and the conversion of ethane.

Although the ethanol and methanol selectivities are not high, the combined formaldehyde–acetaldehyde–methanol–ethanol (FAME) selectivities could be very high. If the ethane conversion is controlled at below 3.5%, the FAME selectivity can reach over 90%. High FAME selectivity (over 85%) can be obtained by operating at lower reaction temperature (252–280°C), lower $O_2$ concentration (5–6%) and shorter residence time ($\approx$6 min).

The $C_2H_5OH$ and FAME selectivities and the E/M ratio increased with decrease in the conversion of ethane, whereas the $CH_3OH$ selectivity passed through its maximum value as the conversion of ethane decreased. The yields of $C_2H_5OH$, $CH_3OH$ and FAME reached their highest values at almost the same ethane conversion level ($\approx$4.5%).

The conversion of ethane increased with increase in concentration of ozone in $O_2$. The minimum ozone concentration in $O_2$ at which the effect of sensitization could be observed was less than 1 wt%. There is a possibility that ozone sensitized ethane–oxygen reactions can be conducted at a higher pressure (e.g., 3–5 atm) if the concentration of ozone generated in $O_2$ can reach more than 1 wt%.

The reaction proceeded by a free radical mechanism. At lower reaction temperature, the reaction was initiated by ozone and at higher reaction temperature, the reactions proceeded by both the ozone initiation reaction and the ordinary homogeneous reaction with dioxygen.

Since higher pressurfavoursrs ethanol formation, we are presently attempting to produce $O_3$ at higher pressure.

## 6. Acknowledgements

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## 7. References

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