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The direct oxidation of ethane to alcohols at high pressures

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Abstract

The oxidation of ethane to ethanol and methanol has been studied at 34 atm. The best result obtained was the total alcohol selectivity of 57% at ethane conversion of 6.2%. The liquid collected contained 37% of methanol and 17% of ethanol. The effect of reaction variables on product distribution and alcohol selectivity and the effect of pre-heater have been examined. The selectivity for ethanol was particularly sensitive to reaction parameters, while the selectivity of methanol formation of 25–30% has been found for wide range of reaction conditions. At high temperatures the transition to oxidative coupling of ethane with *n*-butane formation as the major product (selectivity up to 33%) was observed. Due to the formation of alcohols and butane the process studied has the potential for the production of octane enhancers such as MTBE and ETBE. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Ethane oxidation; Methanol; Ethanol; *n*-butane formation

1. Introduction

The direct conversion of alkanes of natural gas into alcohols is a promising process to produce more valuable chemicals and this process has been studied since the turn of the century. The direct conversion of methane to methanol at high pressures has been extensively studied, see reviews [1,2], while comparatively little has been reported on the conversion of ethane to alcohols. Initial interest was focused on the gas phase oxidation of ethane conducted by Newitt and co-workers [3–5], and the selectivity to ethanol was improved to 62% in a flow system at 100 atm. But the interest in the oxidation of ethane to alcohols subsided after this period, while the mechanism of ethane oxidation in the gas phase with formation of alcohols has been studied by Nalbandyan's group [6,7].

We have recently reported [8] on the homogeneous partial oxidation of ethane at different pressures up to 100 atm. The liquid product collected was a complex mixture of ethanol, methanol and water with minor quantities of other oxygenated products and the total alcohol concentration up to 60% was obtained. The maximum ethanol/methanol ratio (E/M) of six was observed at the highest pressure studied.

In the present investigation we have extended the study of this reaction towards a more detailed and quantitative analysis of reaction products, including the gaseous products. The second part of this study was concerned with the optimal conditions of methanol and ethanol formation and the effect of reaction variables and pre-heater on product distribution.

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2. Experimental

The basic apparatus has been previously described [9]. All experiments were performed in a Pyrex lined stainless steel high-pressure reactor divided into two independently heated zones, a pre-heater zone and a reaction zone. The length of the heating zone was 10 cm for the oven and 11 cm for pre-heater. The pressure of 34 atm was maintained constant by a back-pressure regulator for all experiments. This pressure was close to a maximal pressure available without heating the ethane supply cylinder and connecting lines. Ethane and oxygen, both supplied by Matheson, were used in the experiments. The dual flow control lines (Brooks 5800 series mass flow controllers) allowed the oxygen and ethane to be mixed in a Teflon and quartz wool-packed cross prior to entering the reactor. The reactor was mounted vertically in a thermobox, which was maintained at 120°C.

The products were detected and analysed by on-line gas chromatography using TC and FID detectors, 13X and Porapak Q columns. The condensable products were collected in a cold trap filled with chilled ethanol at near −70°C and also analysed. The identity of products was confirmed by GC–MS analysis (Finnigan Mat) equipped with a DB-5 capillary column.

3. Results and discussion

The results of on-line gas phase analysis for 11 selected experiments are given in Table 1 and will be discussed below. All experiments were performed at oxygen conversion level close to 100%. At lower oxygen conversion the selectivity to partial oxidation products dropped, as it has also been found for methane oxidation at high pressures [9,10]. The results of analysis of liquid product obtained for the same experiments are shown in Table 2. These results were in good conformity with those obtained from on-line analysis. It is necessary to note that the intensive gas evolution from liquid was observed, when the trap with liquid condensate was removed from the chilled ethanol. The GC and GC–MS analysis detected propane and basically *n*-butane in the gas evolved. The main products detected in the gas phase and liquid were methanol, ethanol, CO_x (predominantly CO), water, methane, ethylene, propane, *n*-butane, formaldehyde and acetaldehyde, formic and acetic acids, dimethoxymethane, dimethyl ether, acetone and hydrogen.

The basic results obtained are the following. The homogeneous oxidation of ethane is a quite selective process to the products of partial oxidation and the selectivity of carbon oxides (CO_x) formation did not exceed 16–28% at O_2 concentration of 3.6–12.8% in the reaction mixture, as one can see in Table 1. But this reaction leads to a wide variety of different products due to the rupture of the C–C bond and the secondary processes in comparison with homogeneous oxidation of methane.

The optimal conditions for selective formation of alcohols were so-called "slow oxidation conditions"

Table 1
The effect of reaction parameters on product selectivity in the direct homogeneous oxidation of ethane to alcohols at 34 atm

Exp.	*T* (°C) oven	*T* (°C) pre- heat	F (ml/s)	O_2 conc. (%)	C_2H_6 conv. (%)	Selectivity (%)[a]								
						C_2H_5OH	CH_3OH	CH_4	CO_x	C_2H_4	C_3H_8	n-C_4H_{10}	Aldehydes	Other
1	286	250	1.1	10.3	9.2	16	22	6	19	2	3	9	7	15
2	333	85	5.3	12.8	10.9	4	10	10	26	10	6	25	5	4
3	425	93	5.3	12.8	12.6	1	3	12	26	11	8	33	3	2
4	375	244	4.3	9.5	8.7	5	15	14	28	5	4	18	4	5
5	287	270	0.1	6.6	6.2	28	29	4	16	1	1	5	5	10
6	320	320	4.5	3.6	3.3	10	31	6	20	4	1	9	12	5
7	320	320	4.4	6.6	5.5	15	24	6	25	2	4	11	7	6
8	360	190	4.5	6.6	5.6	17	30	5	22	1	2	12	9	3
9	345	345	20	5.5	4.7	8	25	8	25	3	4	12	10	3
10	360	360	10	5.5	4.7	8	25	7	22	5	2	12	15	4
11	330	320	2.0	8.4	7.0	16	27	6	25	1	2	8	4	10

Other products – total selectivity of formic acid, acetic acid, dimethoxymethane, dimethyl ether and acetone formation.
[a] Aldehydes – total selectivity of formaldehyde and acetaldehyde formation.

Table 2
The composition of liquid product obtained in the direct homogeneous oxidation of ethane to alcohols at 34 atm

Exp.	T (°C) oven	T (°C) pre- heat	F (ml/s)	O_2 conc. (%)	Composition (mol%)[a]							
					H_2O	C_2H_5OH	CH_3OH	CH_2O	CH_3COH	FA	AA	DMM
1	286	250	1.1	10.3	49.5	10.6	27.0	0.3	3.9	4.0	2.6	2.0
2	333	85	5.3	12.8	75.1	2.9	14.1	4.2	2.1	0.4	0.1	0.9
4	375	244	4.3	9.5	70.1	3.5	20.2	3.7	1.2	0.2	0.1	0.6
5	287	270	0.1	6.6	34.6	17.3	36.9	1.1	2.9	2.0	0.6	2.5
6	320	320	4.5	3.6	41.6	11.7	35.2	7.8	3.0	0.3	0.1	0.1
7	320	320	4.4	6.6	53.0	8.6	28.7	4.0	2.2	0.9	0.3	1.0
8	360	190	4.5	6.6	47.0	9.9	34.7	5.3	2.5	0.2	0.1	0.2
9	345	345	20	5.5	55.6	4.7	28.3	7.7	2.6	0.3	0.1	0.5
10	360	360	10	5.5	53.0	4.8	27.6	9.1	3.8	0.3	0.1	1.2
11	330	320	2.0	8.4	50.5	9.8	31.8	2.0	2.0	1.8	0.3	1.5

[a] FA – formic acid, AA – acetic acid, DMM – dimethoxymethane. Acetone and dimethyl ether were detected in liquid with acetone concentrations of 0.08–0.2 mol% and dimethyl ether concentrations of 0.1–0.3 mol%.

and included the minimal temperature required to reach the complete oxygen conversion, low feed flow rates and low oxygen concentrations. The best result obtained was the total alcohol selectivity of 57% with the value of E/M ratio of 0.47 at ethane conversion of 6.2%, 287°C and oxygen concentration of 6.6%, see experiment 5. The liquid collected in the trap contained 37 mol% methanol and 17 mol% ethanol for that experiment, see Table 2.

At higher temperatures and feed flow rates the selectivity of alcohols formation decreased. The higher selectivity to CH_4 and C_1 compounds formation indicates the more intensive ethane cracking, while CO_x formation increased only slightly, when CO selectivity was higher, but CO_2 selectivity dropped. The increased formation of hydrogen and ethylene also indicates that the oxidative dehydrogenation of ethane occurs at elevated temperatures and flow rates.

The ethanol selectivity was particularly sensitive to reaction parameters such as temperature and residence time (feed flow rate) and reduced to a marked degree at higher values of these parameters. The short reaction zone was favourable for higher selectivity of ethanol formation. When the temperature of the pre-heater was the same or very close to that of the oven, we may consider the reactor as having the double length. By comparing experiments 7 and 8, one can see that the selectivity of ethanol formation was higher using short reaction zone, even in spite of increased oven temperature which was necessary to reach the complete oxygen conversion. This effect may be explained by lowering of ethane cracking and ethanol oxidation for short reaction zone.

This effect of reaction variables was less pronounced for methanol formation and methanol selectivity of 25–30% was observed for wide range of reaction conditions, with the exception of high oxygen concentration in the reaction mixture, see Table 1. Methanol selectivity of 25% was found even at high flow rate of 20 ml/s, as can be seen from experiment 9.

Concerning other oxygenated products, the selectivity of acids and dimethoxymethane formation decreases at high flow rates, probably as secondary products. This effect was not pronounced for acetaldehyde, while the formaldehyde selectivity increase may be due to the more intensive ethane cracking. While the selectivity of formation of different oxygenated products was relatively low, the total selectivity of formation was 5–22% and total concentration in liquid product was 6–15%. The formation of these oxygenates leads to a lower alcohol selectivity.

It should be noted that it was extremely complex to maintain a constant temperature at high oxygen concentrations and the temperature oscillations of up to 80°C were observed at high flow rates and 12.8% of oxygen concentration.

Operating with a pre-heater had a beneficial effect for alcohol production from ethane due to a lowering of minimal reaction temperature required for complete oxygen conversion. Earlier the same effect has been found for methane oxidation at high pressures [9].

The presence of *n*-butane in the reaction products was interesting suggesting ethyl radical recombination

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$$

The transition to oxidative coupling of ethane was observed at higher temperatures with selectivity of *n*-butane formation up to 33% at 425°C and was accompanied by higher rates of CH_4, C_2H_4 and propane formation. Remarkably, the selectivity of *n*-butane formation was relatively high in comparison with other products, see Table 1, with the exception of slow oxidation conditions. The very similar behaviour has been observed for methane oxidation at high pressures, namely, the transition to formation of recombination product ethane [9].

In view of the formation of alcohols and butane, the process studied has the potential for the production of octane enhancers such as MTBE and ETBE, although the optimal reaction conditions are different for the formation of alcohols and *n*-butane. Based on the previous results [8], the higher pressure conditions than were employed in the present study look attractive to increase the selectivity to desirable products and especially that of ethanol formation.

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