

## Non-catalytic pyrolysis of ethane to ethylene in the presence of CO<sub>2</sub> with or without limited O<sub>2</sub>

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**Abstract.** Influence of the presence of CO<sub>2</sub>, which is a mild oxidant, on the performance of the thermal cracking of ethane to ethylene in the absence or presence of limited O<sub>2</sub> at different temperatures (750–900°C), space velocities (1500–9000 h<sup>-1</sup>) and CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> and O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> mole ratios (0–2.0 and 0–0.3 respectively) has been investigated. In both the presence and absence of limited O<sub>2</sub>, ethane conversion increases markedly because of the presence of CO<sub>2</sub>, indicating its beneficial effect on the ethane to ethylene cracking. The increased ethane conversion is, however, not due to the oxidation of ethane to ethylene by CO<sub>2</sub>; the formation of carbon monoxide in the presence of CO<sub>2</sub> is found to be very small. It is most probably due to the activation of ethane in the presence of CO<sub>2</sub>.

**Keywords.** Ethane; ethylene; thermal cracking of ethane; ethane cracking in presence of CO<sub>2</sub>; ethane cracking in presence of CO<sub>2</sub> and limited O<sub>2</sub>.

### 1. Introduction

Ethylene, which is a cornerstone in the petrochemical industry, is produced commercially by thermal cracking of ethane, ethane–propane mixture or naphtha in the presence of steam.<sup>1</sup> This process is highly endothermic, energy-intensive and also involves extensive coke formation. The large amount of coke deposited on the inner walls of the tubular cracking reactor creates serious problems, such as reduction in the rate of heat transfer from reactor walls. This in turn requires a higher wall temperature (up to 1100°C) to achieve desirable ethane conversion, which increases the energy demand and also reduces the life of the reactor tubes. It also requires process shut-down for physically removing the coke. Moreover, the ethane conversion achieved is less than about 70%, thus requiring a large recycle of the unconverted ethane. In order to overcome these problems we have suggested earlier to carry out ethane and propane thermal cracking reactions in the presence of limited oxygen.<sup>2–4</sup> By carrying out the thermal cracking of ethane, propane or C<sub>2</sub>–C<sub>4</sub> hydrocarbons from natural gas in the presence of steam and limited oxygen, not only the energy requirement is drasti-

cally reduced but also the coke formation is eliminated or drastically reduced and also the hydrocarbon conversion much above 70% could be obtained. Also in the presence of oxygen, the thermal cracking of ethane/propane is enhanced because of the change in the hydrocarbon activation mechanism and hence the oxy cracking process could be carried out at a much lower temperature and/or contact time than that required for achieving the same conversion in the thermal cracking process.

Carbon dioxide (a greenhouse gas) can also act as a mild oxidant. Utilization of carbon dioxide in catalytic methane partial oxidation reactions, such as catalytic CO<sub>2</sub> reforming of methane<sup>5</sup> and oxidative coupling of methane,<sup>6</sup> and also in the catalytic oxidative dehydrogenation of ethane<sup>7–13</sup> or propane<sup>14</sup> has been reported earlier. It is also interesting to use CO<sub>2</sub> as an oxidant, instead of oxygen or even in the presence of limited oxygen, in the non-catalytic (thermal) hydrocarbon cracking processes for the production of ethylene and other olefins. The present investigation was undertaken for this purpose. The non-catalytic cracking of ethane at atmospheric pressure in the presence of CO<sub>2</sub> at different CO<sub>2</sub>/ethane ratios (0–2.0) with or without oxygen (O<sub>2</sub>/ethane ratio = 0 to 0.3) has been thoroughly investigated at different temperatures (750–900°C) and

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space velocities (1500–9000 h<sup>-1</sup>) in the absence of steam in the feed.

## 2. Experimental

Non-catalytic ethane-cracking reactions were carried out in a continuous-flow quartz reactor.<sup>4</sup> The reactor has low dead volume. The reactor was kept in a tubular electric furnace such that the reaction zone was in the constant temperature zone of the furnace. The feed was a mixture of pure ethane and CO<sub>2</sub> with or without oxygen. The thermal cracking of ethane in the presence of CO<sub>2</sub> was carried out at different process conditions (viz. temperature = 750–900°C; CO<sub>2</sub>/ethane = 0–2.0 and GHSV = 1500–9000 h<sup>-1</sup>) with or without oxygen (O<sub>2</sub>/ethane = 0–0.3). All the ratios of feed components are mole ratios. GHSV is defined as the volume of gaseous feed (measured at 0°C and 1 atm pressure) passed through a unit volume of the reactor per hour. The inlet and outlet temperatures of the reactor were measured by chromel–alumel thermocouples similar to that described earlier.<sup>4</sup> The maximum difference in the reactor inlet and outlet temperatures was 7°C. The reactions were carried out by a procedure similar to that described earlier.<sup>15</sup> After the removal of water (formed particularly in oxy-CO<sub>2</sub> ethane cracking) by condensation at 0°C, the feed and products were analysed by an on-line gas chromatograph with a thermal conductivity detector (TCD) and flame ionization detector (FID), using Poropak-Q and Spherocarb columns. The water condensed from the products was weighed.

Formation of O-containing products other than CO, CO<sub>2</sub>, and H<sub>2</sub>O was not observed. Experimental runs with errors in C, H, and O mass balances less than 6% were considered; the runs with higher errors were discarded. Product distribution data are provided for the product stream without CO<sub>2</sub> and water. Product selectivity reported in this investigation is based on the conversion of carbon from ethane to a particular product. It is described as follows.

Product selectivity =  $100 \times [\text{moles of the product formed per hour} \times \text{number of C in the product}] \div [2 \times \text{mole of ethane converted per hour}]$ .

## 3. Results and discussions

### 3.1 Ethane cracking in presence of CO<sub>2</sub>

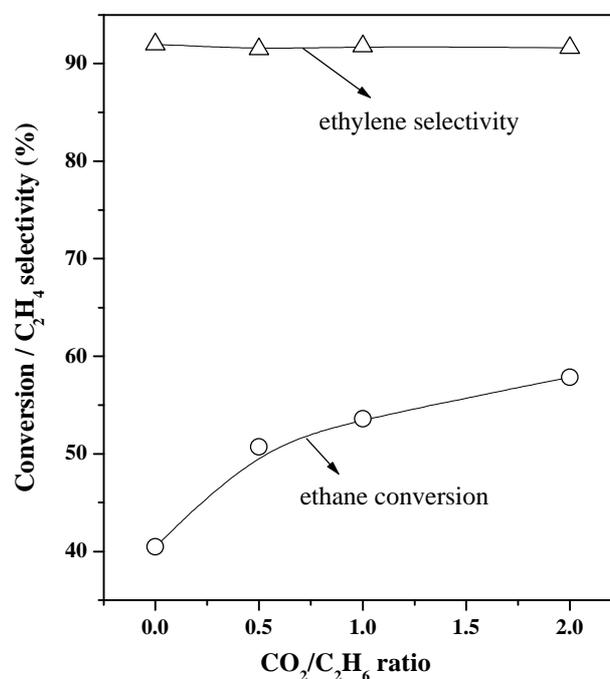
Results showing the influence of CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio in the feed, temperature and gas hourly space velocity

(GHSV, measured at 0°C and 1 atm pressure) on ethane conversion and ethylene selectivity in the cracking of ethane are presented in figures 1–3. Influence of process variables on the distribution (wt. %) of various components (viz. H<sub>2</sub>, CO, methane, ethylene, acetylene, ethane, propylene, propane, C<sub>4</sub> and C<sub>5+</sub> hydrocarbons and benzene) present in the product stream, after the removal of water and CO<sub>2</sub> is given in figure 4.

The results (figure 1) show strong influence of the presence of CO<sub>2</sub> on ethane conversion; it increases with increasing CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio with little or no change in ethylene selectivity. With increase in the CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio, the concentration of ethane in the product stream decreases whereas the concentrations of most of the products increase because of increased ethane conversion. The formation of CO, acetylene, propane, propylene, C<sub>5+</sub> aliphatic and benzene in ethane cracking is however quite small. Since CO<sub>2</sub> is a very mild oxidant, the observed CO formation is expected by the Boudouard reaction,



and/or by the oxidation of highly reactive (partially hydrogenated) carbon species formed in ethane



**Figure 1.** Effect of CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratios on the conversion of ethane and selectivity of ethylene in the CO<sub>2</sub> cracking of ethane at 850°C [GHSV = 6000 h<sup>-1</sup>].

cracking. No coke deposition on the reactor walls is observed and this may be due to the complete oxidation of the carbon and/or coke precursors (partially hydrogenated carbon species) by CO<sub>2</sub>.

Results showing the strong influence of the CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio on the conversion of ethane by reaction 1, purely by its thermal cracking are presented in table 1. Since there is very little or no conversion of ethane by its oxidation with CO<sub>2</sub>, the observed ethane conversion is mainly due to the thermal cracking of ethane even at very high CO<sub>2</sub> concentration in the feed (CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> = 2.0). The results reveal that the rate of ethane thermal cracking is enhanced markedly because of the presence of CO<sub>2</sub>. This observation is quite similar to that reported by us earlier in case of non-catalytic ethane or propane cracking in presence of limited O<sub>2</sub>.<sup>2,4</sup> It appears that ethane is activated by CO<sub>2</sub> at the high reaction temperature (850°C), enhancing the rate of C–C bond cleavage and forming two methyl radicals, which are the primary products formed in the thermal cracking of ethane.

The results in figure 4a show that the concentration of ethane in the product stream, after the removal of CO<sub>2</sub>, decreases while those of all the products in-

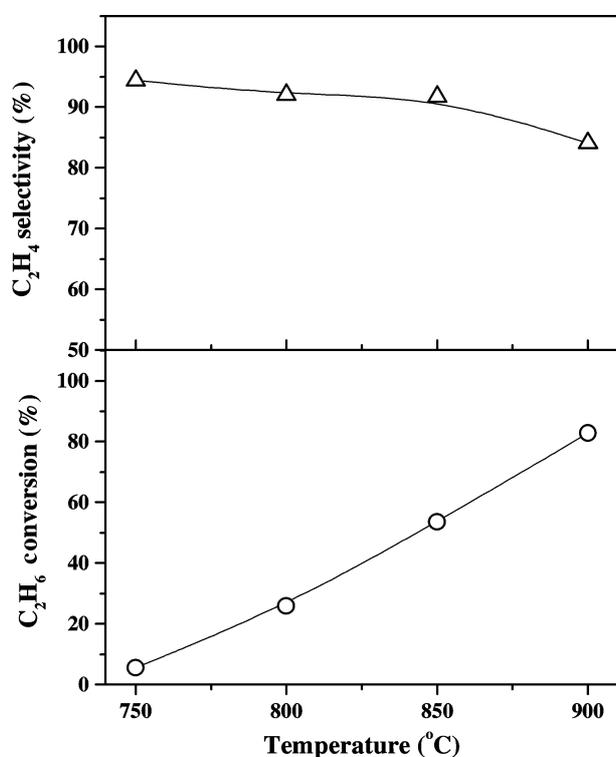
creases on increasing the CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio. This is expected because of the increase in ethane conversion.

On increasing the temperature (from 750 to 900°C), ethane conversion increases (from about 5% to about 80%) almost exponentially. The selectivity of ethylene, however, decreases from about 95% to 85%; the decrease is greater at the higher temperature (900°C).

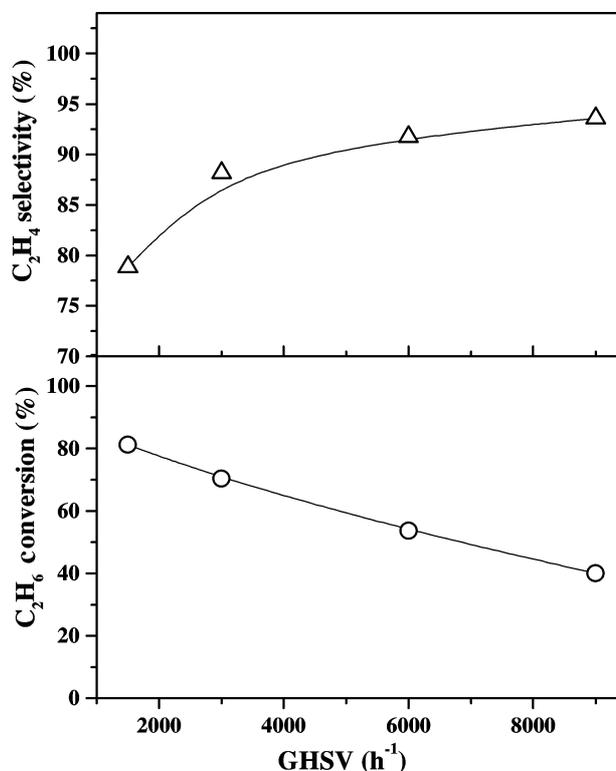
Decrease in the ethylene selectivity on increasing the temperature is because of the fact that the concentration of ethylene in the product stream (without CO<sub>2</sub>) increases almost linearly a increasing the temperature but increase in the formation of methane, C<sub>4</sub> hydrocarbon and benzene is exponential, as shown in figure 4b. Increase in the H<sub>2</sub> concentration is, however, almost linear.

Results in figure 3 show that, as expected, ethane conversion is decreased and ethylene selectivity is increased on increasing the GHSV.

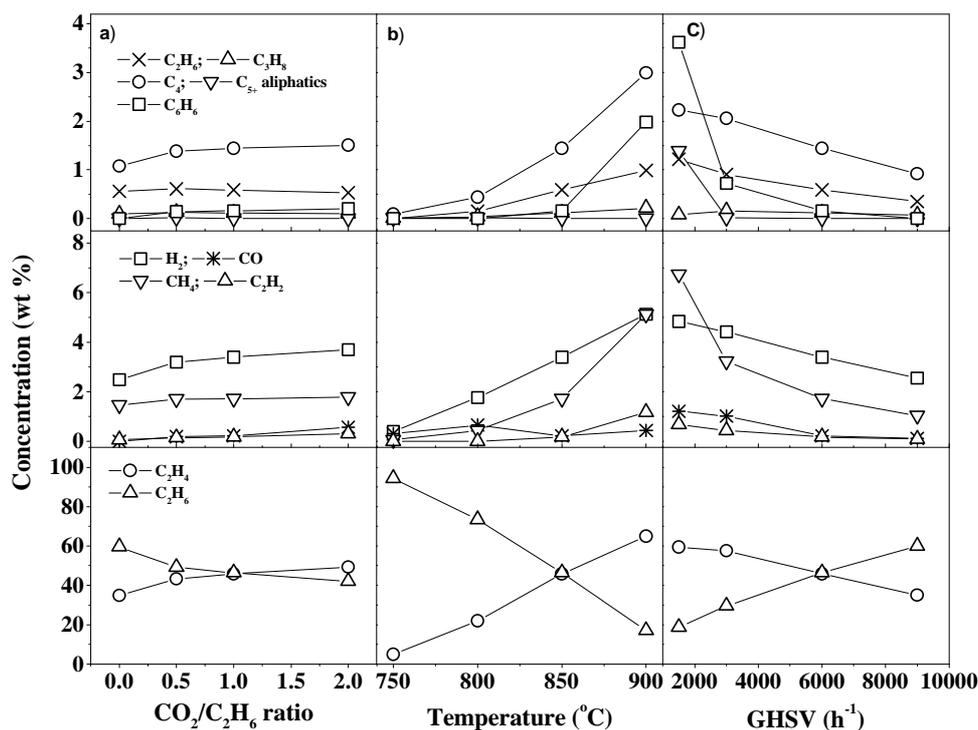
The product distribution shown in figure 4c indicates that the concentration of methane, C<sub>4</sub> hydrocarbon, and benzene in the product stream decreases exponentially, while that of the other products decreases almost linearly on increasing the space velocity.



**Figure 2.** Effect of temperature on the conversion of ethane and selectivity of ethylene in the CO<sub>2</sub> cracking of ethane [GHSV = 6000 h<sup>-1</sup>; CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> = 1.0].



**Figure 3.** Effect of GHSV on the conversion of ethane and selectivity of ethylene in the CO<sub>2</sub> cracking of ethane at 850°C [CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> = 1.0].



**Figure 4.** Influence of (a)  $\text{CO}_2/\text{C}_2\text{H}_6$  ratio (at  $850^\circ\text{C}$ ,  $\text{GHSV} = 6000 \text{ h}^{-1}$ ), (b) reaction temperature ( $\text{CO}_2/\text{C}_2\text{H}_6 = 1.0$  and  $\text{GHSV} = 6000 \text{ h}^{-1}$ ) and (c) space velocity (at  $850^\circ\text{C}$ ,  $\text{CO}_2/\text{C}_2\text{H}_6 = 1.0$ ) on product distribution (without  $\text{CO}_2$  and water) in the  $\text{CO}_2$  cracking of ethane.

**Table 1.** Influence of the presence of  $\text{CO}_2$  in feed on the thermal cracking of ethane at  $850^\circ\text{C}$  ( $\text{GHSV} = 6000 \text{ h}^{-1}$ )

$\text{CO}_2/\text{C}_2\text{H}_6$ ratio in feed	Total ethane conversion (%)	Ethane conversion (%)	
		By reaction with $\text{CO}_2$	By ethane cracking
0.0	40.5	0.0	40.5
0.5	50.7	0.2	50.5
1.0	53.6	0.3	53.3
2.0	57.9	0.5	57.4

### 3.2 Ethane cracking in presence of $\text{CO}_2$ and limited $\text{O}_2$

Results on the conversion of ethane and  $\text{O}_2$  and ethylene selectivity in the thermal cracking of ethane in the presence of  $\text{CO}_2$  and limited  $\text{O}_2$  ( $\text{O}_2/\text{C}_2\text{H}_6 = 0.25$ ) at different  $\text{CO}_2/\text{C}_2\text{H}_6$  ratios (0–2), temperatures ( $750$ – $900^\circ\text{C}$ ) and space velocities ( $\text{GHSV}$  from  $3000$ – $10,000 \text{ h}^{-1}$ ) are presented in figures 5–7. Product distribution and influence of process parameters on the variation in the concentrations of different hy-

drocarbons,  $\text{CO}$  and  $\text{H}_2$  in the product stream (without  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$ ) have been given in figure 8.

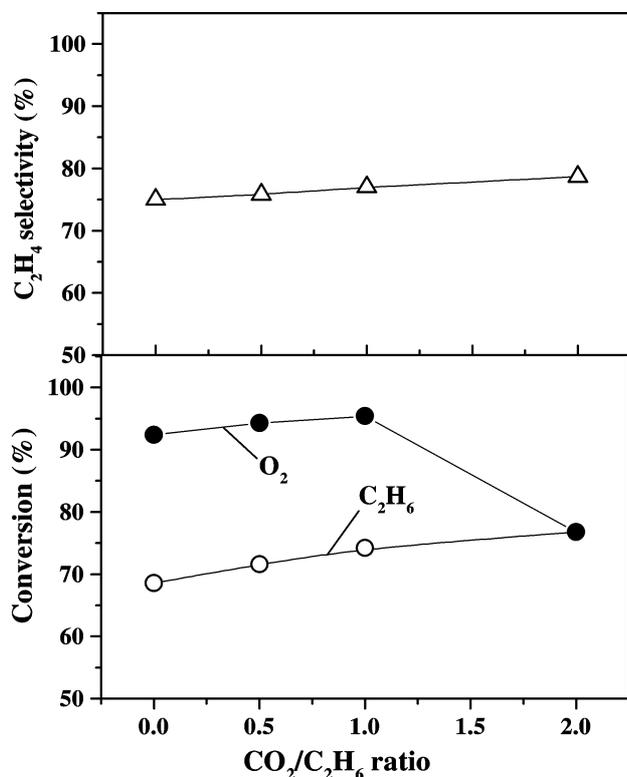
Comparison of these results (figures 5–7) with those obtained in the absence of  $\text{O}_2$  (figures 1–3) shows that, in the presence of both  $\text{CO}_2$  and limited  $\text{O}_2$ , ethane conversion is higher but ethylene selectivity is lower as compared to the results obtained in the presence of  $\text{CO}_2$  alone (i.e. in the absence of limited  $\text{O}_2$ ) due to the formation of  $\text{CO}$  from ethane partial combustion to an appreciable extent (figure 8). There is also some possibility of  $\text{CO}_2$  formation,

which, however, could not be determined because of the high CO<sub>2</sub> concentration in the feed. Earlier studies on the oxy cracking of ethane in the presence of limited O<sub>2</sub> have indicated that the formation of CO<sub>2</sub> as compared to CO in the process is very small.<sup>2</sup>

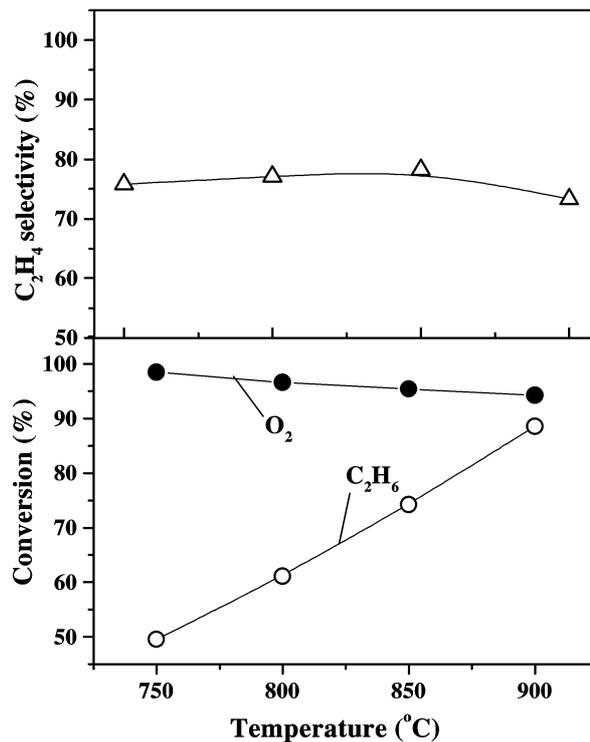
The results in figure 5 show that, as in the presence of CO<sub>2</sub> alone, the ethane conversion increases increasing the CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio. However, unlike in the presence of CO<sub>2</sub> alone, ethylene selectivity also increases significantly, the increase being almost linear. O<sub>2</sub> conversion is, however, passed through a maximum with increase in the CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio.

On increasing the temperature from 750 to 900°C, ethane conversion increases linearly from 50% to 90%, but there is a small decrease in O<sub>2</sub> conversion (from 98% to 94%) (figure 6). The ethylene selectivity, however, first increases and then passes through a maximum at about 850°C on increase in temperature. The formation of different products is also strongly influenced by the temperature, as shown in figure 8b.

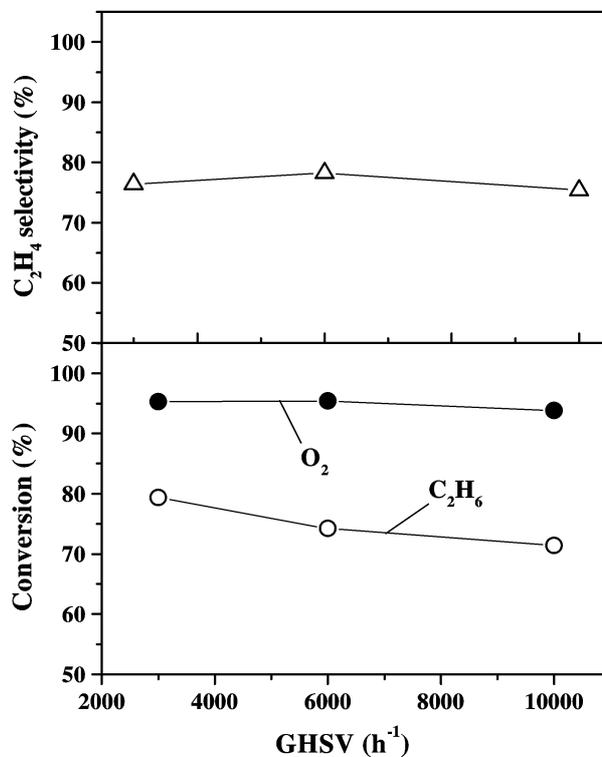
Unlike in the presence of CO<sub>2</sub> alone, the influence of GHSV on the conversion and selectivity in ethane-



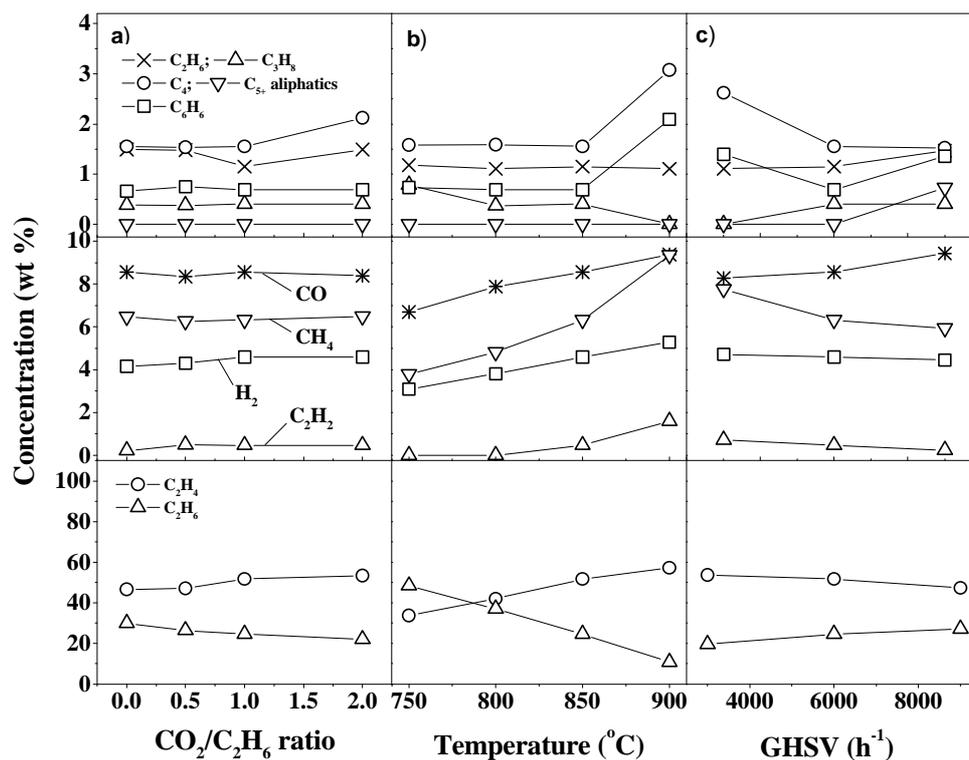
**Figure 5.** Effect of CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio on the conversion of ethane and selectivity of ethylene in the pyrolysis of ethane in the presence of CO<sub>2</sub> and limited O<sub>2</sub> at 850°C [O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> = 0.25; GHSV = 6000 h<sup>-1</sup>].



**Figure 6.** Effect of temperature on the conversion of ethane and selectivity of ethylene in the pyrolysis of ethane in the presence of CO<sub>2</sub> and limited O<sub>2</sub> [O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> = 0.25; CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> = 1.0; GHSV = 6000 h<sup>-1</sup>].



**Figure 7.** Effect of GHSV on the conversion of ethane and selectivity of ethylene in the pyrolysis of ethane in the presence of CO<sub>2</sub> and limited O<sub>2</sub> at 850°C [O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> = 0.25; CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> = 1.0].



**Figure 8.** Influence of (a)  $\text{CO}_2/\text{C}_2\text{H}_6$  ratio (at  $850^\circ\text{C}$ ,  $\text{GHSV} = 6000 \text{ h}^{-1}$ ), (b) reaction temperature ( $\text{CO}_2/\text{C}_2\text{H}_6 = 1.0$  and  $\text{GHSV} = 6000 \text{ h}^{-1}$ ) and (c) space velocity (at  $850^\circ\text{C}$ ,  $\text{CO}_2/\text{C}_2\text{H}_6 = 1.0$ ) on product distribution (without  $\text{CO}_2$ , water and oxygen) in the oxy- $\text{CO}_2$  cracking of ethane ( $\text{O}_2/\text{C}_2\text{H}_6 = 0.25$ ).

cracking in the presence of both  $\text{CO}_2$  and limited  $\text{O}_2$  is small and consequently that on the product distribution is also small, as shown in figure 8c.

### 3.3 Reaction involved in the thermal cracking of ethane in the presence of $\text{CO}_2$ with or without limited $\text{O}_2$

In the presence of  $\text{CO}_2$  alone, the reactions involved in the ethane cracking are expected to be similar to those involved in conventional ethane cracking (ethane cracking is initiated by C–C bond cleavage,  $\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$ ) except the fact that ethane is activated in the presence of  $\text{CO}_2$ . However, in the presence of both  $\text{CO}_2$  and limited  $\text{O}_2$ , mechanism and reaction involves are both expected to be similar to that in the oxy cracking of ethane (in the presence of  $\text{O}_2$ , ethane cracking is initiated by the abstraction of H from ethane molecule by  $\text{O}_2$  with the formation of ethyl radical,  $\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5 + \text{HO}_2$ ).<sup>2</sup>

Ethane cracking in the presence of  $\text{CO}_2$  is a highly endothermic process. However, ethane cracking in the presence of both  $\text{CO}_2$  and limited  $\text{O}_2$  can be mildly

exothermic, mildly endothermic or thermo neutral, depending upon the process conditions, as in case of oxy cracking of ethane described earlier,<sup>2</sup> because of coupling of the simultaneously occurring endothermic ethane cracking and exothermic ethane oxidation (mostly to  $\text{CO}$  and  $\text{H}_2\text{O}$ ) reactions in the process, leading to energy saving to a large extent.

## 4. Conclusions

From the above studies, the following important conclusions can be drawn.

- (1) The presence of  $\text{CO}_2$  in both thermal and oxy-cracking of ethane has a beneficial effect.
- (2) In both cases, ethane conversion increases with increasing  $\text{CO}_2/\text{C}_2\text{H}_6$  ratio in the feed; ethane seems to be activated in the presence of  $\text{CO}_2$ .
- (3) At different process conditions, ethane conversion is higher but ethylene selectivity is lower when limited  $\text{O}_2$  is added to the ethane- $\text{CO}_2$  feed because of the formation of  $\text{CO}$  due to partial combustion of ethane. However, in the presence of both  $\text{CO}_2$  and

O<sub>2</sub>, the process is expected to become highly energy efficient with large energy saving for coke-free ethylene production from ethane.

### Acknowledgment

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