Coupling of Thermal Cracking with Noncatalytic Oxidative Conversion of Ethane to Ethylene

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Homogeneous thermal cracking of ethane, which is an endothermic and hence energy-intensive process, was carried out in the presence of limited O_2 under different process conditions (at 600°–850°C; O_2/ethane ratio of 0–0.2; H_2O/ethane ratio of 0–3.3; and space velocity of 2,000–11,000 h^{-1}). The influence of a sulfur additive in the feed and reactor material on the process performance was also investigated. Noncatalytic oxycracking of ethane in the presence of limited O_2, greatly enhances not only the total conversion of ethane but also the conversion of ethane by purely thermal cracking. This process also occurs at a much lower contact time than that required to achieve the same conversion for the thermal cracking process. Also, both the exothermic oxidative conversion and the endothermic thermal cracking of ethane occur simultaneously, which makes this process very energy-efficient, with a drastic reduction in external energy requirement and coke formation. By manipulating the process conditions, particularly the temperature and O_2/C_2H_6 ratio, the overall process can be made almost thermoneutral, mildly exothermic, or mildly endothermic.

Introduction

Ethylene (which is the keystone of the petrochemical industry) is produced from ethane, an ethane–propane mixture, or naphtha by thermal (noncatalytic) cracking in the presence of steam (Kniel et al., 1980). However, the thermal-cracking process is highly endothermic, and hence consumes a lot of external energy and produces a large amount of coke. The extensive coke deposits on the inner walls of the tubular cracking reactor cause serious problems such as reduced heat transfer from the reactor walls. This in turn requires a higher wall temperature (up to 1,100°C) which increases the energy demands and reduces the life of the reactor tubes. The reactor must therefore be shut down so the coke can be removed. In order to overcome these problems, studies have recently been made throughout the world by many workers in the area of heterogeneous catalytic oxidative dehydrogenation of ethane to ethylene (Argent and Harris, 1986; Morales and Lunsford, 1989; Erdohelyi and Solymosi, 1990; Conway and Lunsford, 1991; Kennedy and Cant, 1991; Swaan et al., 1992; Desponds et al., 1993; Huff and Schmidt, 1993; Zhang et al., 1993; Burch and Crabb, 1993). We have also very recently studied the coupling of the thermal cracking with the heterogeneous catalytic oxidative conversion of ethane to ethylene, using a diluted catalyst (Choudhary et al., 1995). Studies have also been reported in the literature on the homogeneous (noncatalytic) oxidation of ethane (Burch and Crabb, 1993; Choudhary and Rane, 1992; Gray, 1953; Gray et al., 1984; Choudhary and Rajput, 1995). At low temperature and high oxygen concentration, an unsteady/oscillatory reaction behavior has been observed (Gray et al., 1984; Choudhary and Rajput, 1995).

From a practical standpoint, it is very important to improve the performance of the currently used thermal cracking process and also to greatly reduce its energy requirement. This investigation was therefore undertaken with the following objectives: (1) to carry out the thermal (noncatalytic) cracking of ethane to ethylene, not only in the presence of steam, but also in the presence of limited oxygen, to reduce coke formation during the process, thus allowing the process to become highly energy efficient, which results in a large energy saving due to the simultaneous occurrence of noncatalytic homogeneous exothermic oxidative conversion and endothermic thermal cracking reactions of ethane; and (2) to study the effect of the addition of the sulfur compound (in ppm) in the feed on ethylene selectivity and also on coke

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formation in the absence and presence of Inconel metal alloy, a material commonly used in the construction of ethane cracking reactors.

Experimental

The noncatalytic ethane conversion reactions were carried out in two continuous-flow quartz reactors as shown in Figure 1. The reactors have low dead volume. Both reactors were kept in tubular electric furnaces such that their reaction zone was in the constant temperature zone of the furnace. Reactor A was used for studying the influence of various process variables (viz., temperature, O_2/C_2H_6, and H_2O/C_2H_6 mole ratios in the feed and space velocity) on the conversion, selectivity, and net heat of reaction in the oxycracking of ethane. On the other hand, reactor B was used to study the influence of sulfur compounds (viz., thiophene) on the feed, as well as the effect of Inconel-800 metal alloy on the conversion and selectivity in the ethane oxycracking process. The alloy tube (open at both ends) was inserted in the reactor as shown in Figure 1b. The gaseous feed flowed both inside and outside the hallow tube. The feed was a mixture of pure ethane and steam with or without oxygen and the sulfur compound. The space velocity was measured at 0°C and 1 atm (101.3 kPa) pressure. The axial temperature in reactor A and the inlet and outlet temperature of reactor B were measured by Chromel–Alumel thermocouples, as shown in Figure 1. Both reactors were isothermal; the maximum temperature gradient observed was 5°C. The noncatalytic reactions were carried out by a procedure similar to that described earlier (Choudhary et al., 1991). The feed and products (after separating water by condensation at 0°C) were analyzed by an on-line gas chromatograph, using a Poropak-Q and Spherocarb columns. The error in C, H, and O mass balance was less than 5%.

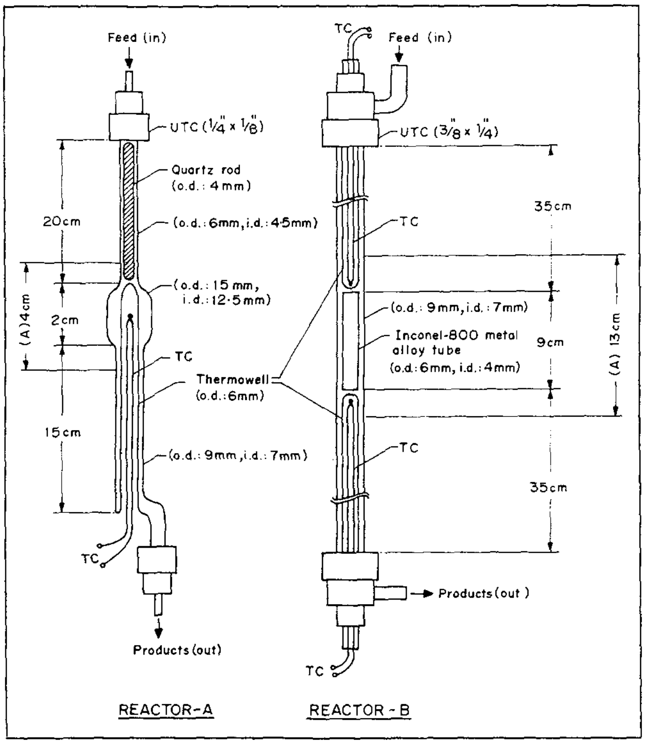

Figure 1. Quartz reactors used for the oxycracking of ethane.

TC = thermocouple; UTC = ultra-torr connector; A = constant temperature zone of tubular electric furnace used for the reactors.

Results and Discussion

Enhancement in thermal cracking of ethane

Conversions of ethane by thermal cracking in the presence and absence of oxygen at different temperatures, space velocities, and O_2/C_2H_6 feed ratios are compared in Table 1. The conversion of ethane by purely thermal cracking was estimated through an oxygen balance by subtracting the conversion due to the formation of CO, CO_2, and H_2O in the oxidative dehydrogenation of ethane from the total conversion. The comparison shows that, in the presence of limited O_2, not only is the total conversion of ethane much higher than that observed in the absence of O_2, but so is its conversion by thermal cracking alone. The enhancement in ethane thermal cracking is, however, very large at lower temperatures (below 800°C); in general, the enhancement is decreased by increasing the reaction temperature. A highly probable explanation for this is given below. In the presence of limited O_2, the ethane conversion reaction at lower temperatures is initiated by the well-known free radicals forming reaction,

$$C_2H_6 + O_2 \rightleftharpoons C_2H_5^{\cdot} + HO_2^{\cdot}, \qquad (1)$$

which has much lower activation energy [51 kcal·mol^{-1} (Chen et al., 1991)] than that [89.0 kcal·mol^{-1} (Chen et al., 1991)] of the chain initiation reaction,

$$C_2H_6 \rightleftharpoons C_2H_5^{\cdot} + H^{\cdot}, \qquad (2)$$

involved in the thermal cracking of ethane in the absence of O_2. Because of the presence of limited O_2, the unimolecular cracking of the ethyl radicals,

$$C_2H_5^{\cdot} \rightleftharpoons C_2H_4 + H^{\cdot}, \qquad (3)$$

Table 1. Ethane Conversion by Purely Thermal Cracking in the Presence and Absence of Oxygen in the Feed*

Temp. (°C)	O_2/C_2H_6 Mol Ratio in Feed	Space Vel. (h^{-1})	Total Conv. (%)	Conv. by Thermal Cracking: Presence of O_2 (%)	Conv. by Thermal Cracking: Absence of O_2 (%)
600	0.14	3,700	21.2	12.2	0.0
650	0.14	3,700	25.3	15.4	0.0
700	0.14	3,700	36.6	21.1	4.2
750	0.14	3,700	48.8	33.9	18.9
650	0.10	7,420	17.0	4.1	0.0
700	0.10	7,420	28.8	15.5	2.4
750	0.10	7,420	42.2	30.1	15.7
800	0.10	7,420	59.1	47.7	36.6
700	0.14	11,050	31.5	11.0	2.1
750	0.14	11,050	43.0	26.6	7.7
800	0.14	11,050	60.7	44.2	28.5
700	0.20	7,420	39.0	15.2	2.4
750	0.20	7,420	48.9	27.5	15.7

*Steam/ethane mol ratio in feed = 1.0.

which has much lower activation energy [41.1 kcal·mol^{-1} (Chen et al., 1991)] than reaction 2, also occurs simultaneously with the oxidative reaction,

$$C_2H_5^{\cdot} + O_2 \rightleftharpoons C_2H_4 + HO_2^{\cdot}. \tag{4}$$

Also, more ethyl radicals from ethane are formed by the pyrolytic chain propagation reaction,

$$C_2H_6 + H^{\cdot} \rightleftharpoons C_2H_5^{\cdot} + H_2, \tag{5}$$

which has a very low activation energy [4.9 kcal·mol^{-1} (Chen et al., 1991)]. Thus, at lower temperatures and in the presence of limited O_2, the elementary pyrolytic reactions (reactions 3 and 5) occur simultaneously with the elementary oxidation reactions (reactions 1 and 4), along with other known free-radical chain propagation and termination reactions (Chen et al., 1991; Geisbrecht and Daubert, 1975), forming methane, C_{3+} hydrocarbons, carbon oxides, and water. The pyrolytic reactions (reactions 3 and 5), followed by the oxidative chain initiation reaction (reaction 1), are responsible for the observed high enhancement in the conversion of ethane purely by its thermal cracking at lower temperatures due to the presence of limited O_2. However, at higher temperatures (above 800°C), reaction 2 also becomes important, causing a decrease in the enhancement in the rate of ethane cracking.

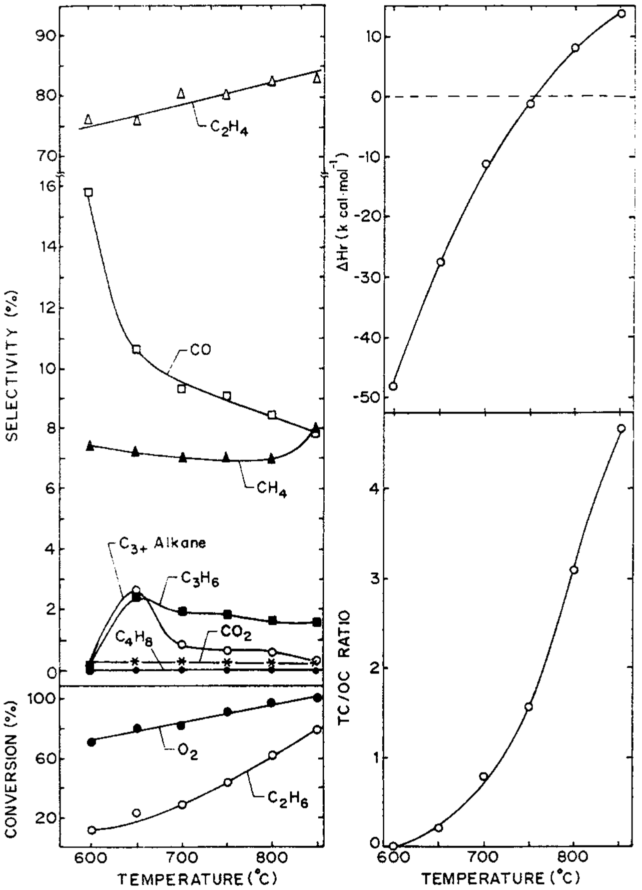

Figure 2. Influence of temperature on the oxycracking of ethane.

$O_2/C_2H_6 = 0.14$; $H_2O/C_2H_6 = 1.0$; GHSV = 7,370 h^{-1}.

No coke or tarlike product formation was observed when the process was carried out with oxygen in the feed. This is probably because the coke precursors (highly reactive unsaturated hydrocarbon species) were oxidized to carbon oxides.

The preceding observations also indicate that, in the presence of limited O_2, both endothermic ethane cracking (which is initiated by reaction 1 and propagated by reaction 3) and exothermic ethane oxidation reactions (involving oxidative conversion of ethyl radicals to ethylene, carbon oxide, and methane) occur simultaneously. This has important practical implications.

Coupling of exothermic and endothermic reactions

Because free-radical reactions 1–4 occur simultaneously there is a coupling of the exothermic oxidative conversion and endothermic thermal cracking reactions of ethane. In order to know the influence of process conditions on the conversion, product selectivity, and occurrence of the thermal cracking of ethane relative to its oxidative conversion and the net heat of the process, the ethane oxycracking process was carried out at different temperatures, O_2/C_2H_6, and steam/C_2H_6 ratios in feed and gas hourly space velocities (GHSV) in the empty quartz reactor (reactor A). The results are given in Figures 2–5. The net heat of the reactions (ΔH_r, expressed in kcal per mole of ethane converted) in the ethane oxycracking process is obtained by subtracting the heat of formation (at the reaction temperature) of the components in the feed from that of the components present in the product

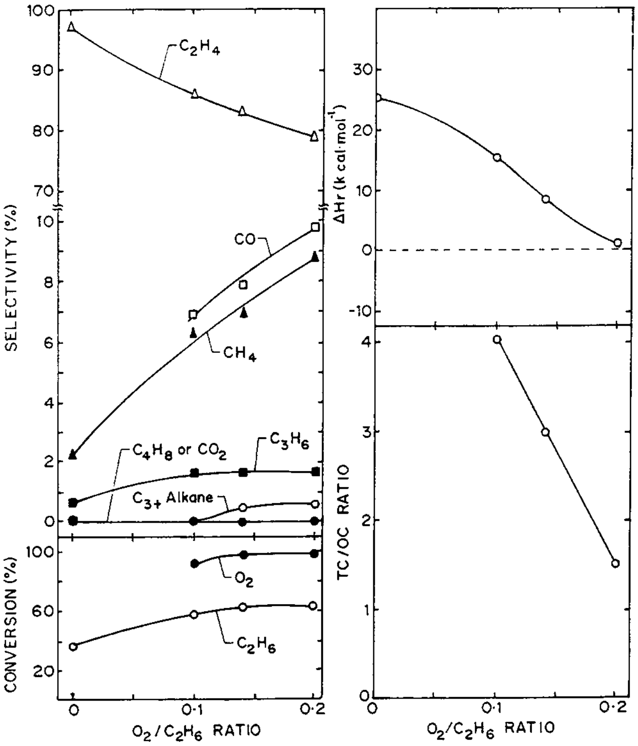

Figure 3. Influence of O_2/C_2H_6 ratio in feed on the oxycracking of ethane at 800°C.

$H_2O/C_2H_6 = 1.0$; GHSV = 7,370 h^{-1}.

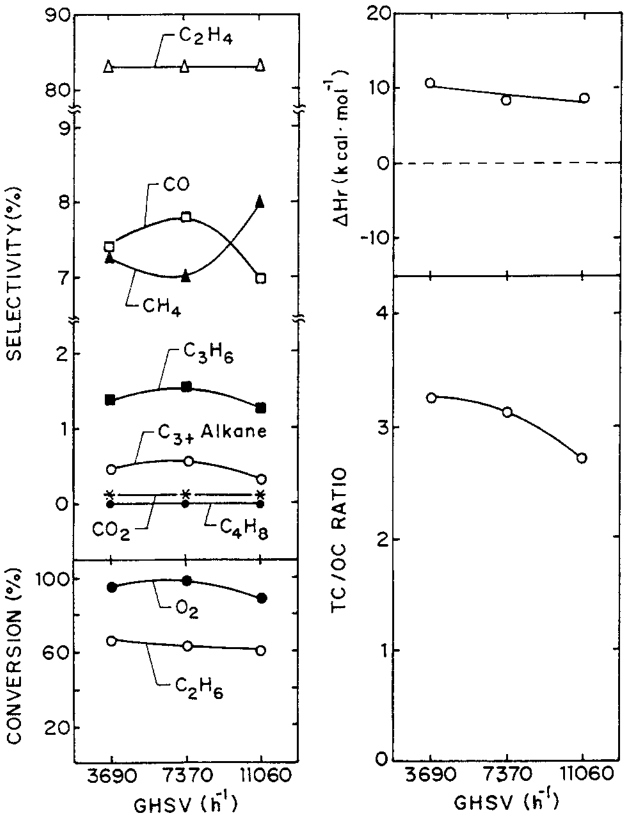

Figure 4. Influence of space velocity on the oxycracking of ethane at 800°C.

$O_2/C_2H_6 = 0.14$; $H_2O/C_2H_6 = 1.0$.

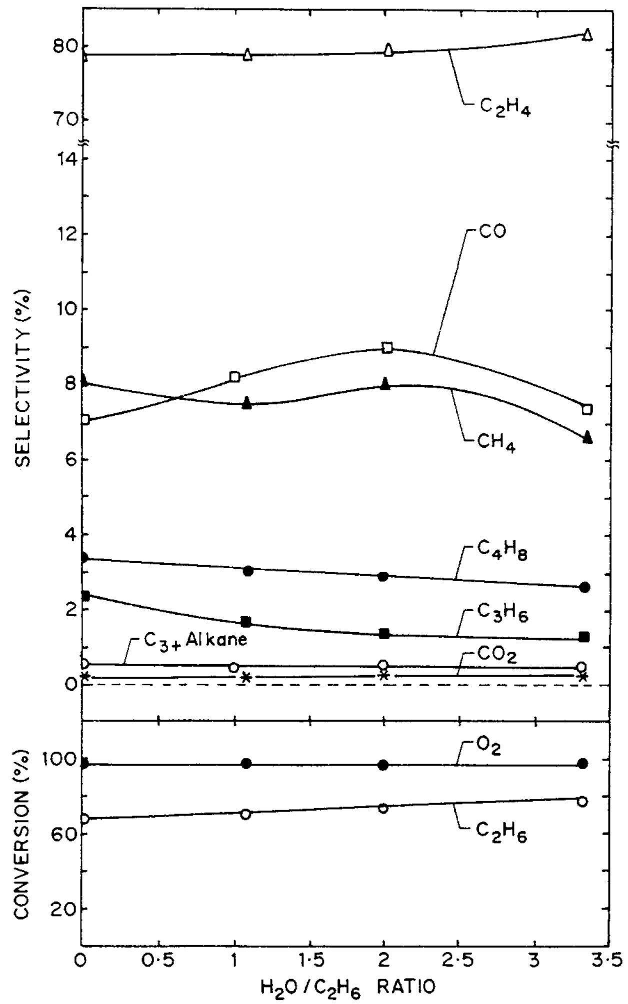

Figure 5. Influence of H_2O/C_2H_6 ratio in the feed on the oxycracking of ethane at 800°C.

$O_2/C_2H_6 = 0.16$; GHSV = 1,970 h^{-1}.

stream. The overall process is exothermic and endothermic when the net heat of reactions (ΔH_r) is negative and positive, respectively.

The results (Figures 2–5) show the following important effects of the process variable on the conversion, selectivity, net heat of reactions, and thermal cracking/oxidative conversion (TC/OC) ratio in the ethane oxycracking process.

As expected, the ethane conversion increases when the temperature (Figure 2) is increased, but decreases when the space velocity is increased (Figure 4); it is increased by increasing the O_2/C_2H_6 ratio (Figure 3). However, the effect of the steam/C_2H_6 ratio on the conversion of both C_2H_6 and O_2 is quite small (Figure 5).

The selectivity for ethylene is increased and that of CO or CO_x is decreased when the temperature is increased (Figure 2), whereas the opposite trend is observed when the O_2/C_2H_6 ratio is increased (Figure 3). However, the space velocity and steam/C_2H_6 ratio have little effect on ethylene selectivity. The influence of the process variables on the selectivity of methane, C_{3+} alkane, and alkene is shown in Figures 2–5.

The net heat of the reactions (ΔH_r) in the process is increased by increasing the temperature (Figure 2). It is, however, decreased by increasing the O_2/C_2H_6 ratio and the space velocity.

The TC/OC reaction ratio is increased, and the heat produced or process exothermicity is decreased markedly when the temperature increases (Figure 2). However, when the O_2/C_2H_6 ratio and space velocity are increased, the exact opposite is seen to occur (Figure 3). In both cases, the TC/OC reaction ratio is decreased, thus increasing the process exothermicity when the O_2/C_2H_6 ratio and the space velocity are increased. The effect of the space velocity on ΔH_r is, however, smaller. The observed variation in the net heat of reactions (ΔH_r) with the process variables is consistent with that observed for the TC/OC reaction ratio (Figures 2–4). Thus, the net heat of the reactions, which are occurring simultaneously in the ethane oxycracking process, can be controlled by manipulating the process conditions, particularly the temperature and concentration of O_2 relative to that of ethane in the feed. The results show that the process conditions can be manipulated to make the process almost thermoneutral, mildly exothermic, or mildly endothermic.

The results (Figures 2–5) reveal that, by carrying out the ethane cracking process in the presence of steam and limited O_2 (the concentration of which is well below the explosion limit), it is possible to convert ethane into ethylene with high conversion ($> 60\%$) and selectivity ($> 80\%$) and also with a large energy saving. As can be seen, the external energy required for the process can be drastically reduced or even eliminated by making the process mildly endothermic, thermoneutral, or mildly exothermic. Further, since the heat produced in the exothermic reactions,

$$C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O + 25.1\ (\text{kcal}\cdot\text{mol}^{-1}\text{ at }800°\text{C}) \tag{6}$$

$$C_2H_6 + 2.5O_2 \rightarrow 2CO + 3H_2O + 206.6\ (\text{kcal}\cdot\text{mol}^{-1}\text{ at }800°\text{C}) \tag{7}$$

$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O + 341.5\ (\text{kcal}\cdot\text{mol}^{-1}\text{ at }800°\text{C}) \tag{8}$$

$$C_2H_5^{\cdot}, C_2H_4 \xrightarrow{O_2} CO, CO_2, CH_4, \text{ and } H_2O + \text{heat}, \tag{9}$$

is used instantly by the endothermic reaction,

$$C_2H_6 \rightarrow C_2H_4 + H_2 - 34.2\ (\text{kcal}\cdot\text{mol}^{-1}\text{ at }800°\text{C}), \tag{10}$$

occurring simultaneously, the overall process occurs in a most energy-efficient and safe manner without formation of hot spots, and therefore without any explosion hazards.

It may be noted, however, that in the thermal cracking process, selectivity at the same conversion is higher by about 10%. The selectivity gap can be reduced by further developing/improving the coupled process. Nevertheless, the reduced selectivity is the price to be paid for achieving the advantages (viz., lower coke formation, lower contact time or higher productivity, and lesser energy requirement) of the coupled process.

Effect of sulfur compound in the feed and the presence of a metal alloy

Results showing the influence of thiophene in the feed (0–60 ppm) on the distribution of product in the oxycracking of ethane at 845 ± 5°C are presented in Table 2. The results show that because of the addition of thiophene to the feed, the conversion of ethane is decreased only a little, but the concentration of both ethylene and ethane is increased, and that of CO is decreased appreciably. This clearly shows the beneficial effect of the sulfur compound in reducing the formation of CO, thus saving valuable carbon from ethane from its oxidation to CO.

In industrial practice, the ethane oxycracking process is expected to be carried out in a reactor madeup of a metal alloy similar to that used for the ethane thermal cracking process. Hence, it is interesting to know the influence of the metal alloy (Inconel-800) on the selectivity in the ethane oxycracking process. A comparison of the product selectivity in the oxycracking of ethane with and without the Inconel-800 metal alloy tube (in reactor B, Figure 1) for almost the same conversion of ethane (49 ± 2%) and oxygen (70 ± 1%) appears in Table 3. In this case, thiophene, at a concentration of 60 ppm, was added to the feed. The results indicate that the presence of the Inconel-800 metal alloy tube (which was pretreated at 800°C for 4 h with N_2 containing 60 ppm thiophene in the reactor with a very high metal surface/reactor volume ratio (16 cm^{-1}) has very little effect on the product selectivity. It can be noted that in this case the metal surface/reactor volume ratio is much higher than that (about 0.4 cm^{-1}) for the industrial coil reactor (diam. ≈ 10 cm) used in the thermal cracking process. This shows that the oxycracking process can be carried out in the metallic coil reactor without affecting the selectivity for ethylene and higher olefins. Moreover, no carbon was seen to form on the metal alloy tube in the ethane oxycracking process. However, when the cracking of ethane was carried out without oxygen under identical conditions, a significant deposition of carbon (8×10^{-4} $g \cdot h^{-1}$) was observed on the metal alloy tube.

Table 2. Influence of Thiophene in Feed on Product Distribution in Ethane Oxycracking*

	Conc. of Thiophene in Feed (ppm)		
	0.0	18	60
Conversion (%)			
C_2H_6	68.1	67.7	67.5
O_2	96.3	96.1	96.2
Composition of product stream with unconverted reactants (wt. %)			
H_2	3.6	3.4	3.2
CO	9.6	8.0	7.3
CO_2	0.3	0.3	0.3
O_2	0.7	0.7	0.7
CH_4	3.8	3.7	3.6
C_2H_4	48.7	49.9	50.6
C_2H_6	30.0	30.6	30.9
C_3H_6	1.1	1.2	1.2
C_3H_8	0.5	0.5	0.5
C_4H_8	1.2	1.2	1.2
C_4H_{10}	0.4	0.4	0.4
C_{5+}	0.06	0.07	0.08

*Reaction conditions: inlet temperature—851°C; outlet temperature—840°C; GHSV—9,490 h^{-1}; O_2/C_2H_6 mole ratio—0.17; H_2O/C_2H_6 mole ratio—0.47.

Conclusions

By performing the noncatalytic oxycracking of ethane in the presence of limited O_2, not only the total conversion of ethane but also the conversion of ethane purely by its thermal cracking are greatly enhanced. This process therefore occurs at a much lower contact time than that required for the thermal cracking process for achieving the same conversion. Also, both these reactions occur simultaneously, making this process very energy efficient and safe by coupling the

Table 3. Product Selectivity in the Oxycracking of Ethane*

Product	Selectivity (%) Without Inconel-800	Selectivity (%) With Inconel-800
C_2H_4	83.0	83.8
C_3H_6	2.2	1.7
C_3H_8	1.4	1.2
C_4H_8	0.8	0.6
C_2–C_4 olefins	86.0	86.1
C_4H_{10}	2.0	1.9
CH_4	5.0	4.2
CO	5.4	6.1
CO_2	0.2	0.5

*O_2/C_2H_6 = 0.17 and H_2O/C_2H_6 = 0.5 in the absence and presence of Inconel-800 metal alloy tube (metal surface/reactor volume ratio = 16 cm^{-1}) for the ethane conversion of 49 ± 2% and O_2 conversion of 70 ± 1% (concentration of thiophene in feed—60 ppm).

exothermic and endothermic reactions with a drastic reduction in the external energy requirement and in coke formation. The addition of a sulfur compound to the feed has a beneficial effect—it causes an increase in the selectivity for ethylene, but a decrease in the CO selectivity. The presence of the Inconel-800 metal alloy has little or no effect on the selectivity for ethylene and higher olefins, or on carbon formation in the ethane oxycracking process.

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