

OXIDATIVE COUPLING OF METHANE TO ETHYLENE OVER SODIUM PROMOTED MANGANESE OXIDE

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Abstract Manganese oxide catalyst promoted with sodium and supported on silica exhibits fairly good activity and selectivity towards the synthesis of ethylene from methane at the optimum operating conditions. Methane and oxygen were fed into a tubular fixed bed reactor packed with catalyst under atmospheric pressure. The effects of temperature, residence time and feed composition on conversion, selectivity and yield were investigated. Ethane and ethylene (C_2 compound) were obtained with 33% selectivity at a 43% conversion of CH_4 over 3cc of 5 Wt% Na-promoted Mn_2O_3 at $83^\circ C$. In this reaction system both the C_2 selectivity and CH_4 conversion increased with an increase in reaction temperature up to $830^\circ C$.

چکیده زوج شدن اکسیداسیونی متان در حضور کاتالیزور اکسید منگنز همراه با ارتقاء دهنده‌ای (Promoter) از گروه IA (فلزات قلیایی) فعالیت و قدرت انتخاب پذیری خوبی را در سنتز اتیلن نشان داده است. در یک راکتور لوله ای شکل از جنس کوارتز با بسترنایت و در فشار اتمسفریک تأثیر پارامترهای نظیر درجه حرارت، زمان تماس، ترکیب درصد خوراک بر روی میزان تبدیل، بازده و قدرت گزینش پذیری کاتالیزور مورد مطالعه قرار گرفت. این مطالعات نشان داد که در دمای $830^\circ C$ درجه سانتیگراد و فشار اتمسفریک، 43 درصد متان تبدیل به محصول میگردد. درجه گزینش پذیری ترکیبات C_2 برابر با 33 درصد و بازده برابر با $14/2$ درصد میباشد.

INTRODUCTION

Methane which is abundant as the main component of natural gas may be also produced by the hydrogenation of carbon, carbon monoxide or carbon dioxide. High molecular stability however makes it difficult to convert CH_4 into other useful chemicals [1]. The partial oxidation of methane into more reactive chemicals such as methanol, ethylene and other aliphatics is the current significant problem in heterogeneous catalysis. In general it has not been possible to achieve both high conversion of CH_4 and good selectivity for partial oxidation products [2,3].

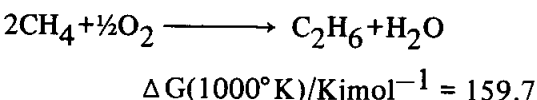
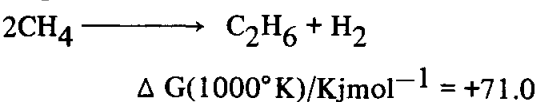
Recently, the oxidative coupling of methane to form ethane and ethylene has been the subject of much extensive research throughout the world [4].

It is a particularly attractive alternative to existing processes such as Fischer-Tropsch [5] and methanol to gasoline [5] (MTG), for the conversion of methane to valuable products, both of which require the expensive process of methane steam reforming to produce synthesis of gas.

Keller and Bhasin [2] were among the first to report the direct conversion of methane to C_2 hydrocarbons. Many studies have been made to find an efficient catalyst under a variety of reaction conditions [6]. Most of the catalysts that have been tested are reducible metal oxides, oxides of rare earth metals or oxides of alkali and alkaline earth metals [7].

Oxidative coupling of methane is preferred to the production of C_2 intermediates by methane oxidation over

solid oxides. Because the dehydrogenative coupling of methane is thermodynamically unfavorable, the reaction is carried out with an oxidant to obtain a favorable free energy [10]:



In methane oxidation in general, the main objective is to achieve high conversions without significant loss of methane to complete combustion [8] but for dimerization the situation may be different. The initial process is the formation of methyl radicals by the loss of hydrogen atoms from methane [9]. Ethane is the primary product, but this can readily undergo dehydrogenation to ethylene. The homolytic bond dissociation energy of ethylene (460 KJ/mole) is higher than CH_4 (439 K/mol) [11,12]. Thus, in reaction pathways that involve homolytic bond breakage, a

situation exists in which a product of methane is formed that is less reactive than methane.

In the present paper we report on the selective conversion of methane to ethylene and ethane at relatively high conversions by using O_2 as the oxidant. C_2H_4 and C_2H_6 are produced by the formation and coupling of methyl radicals over a Na promoted Mn_2O_3 catalyst.

EXPERIMENTAL

Reactions were performed by using single-phase flow reactors, made of fused-silica (quartz) with inside diameters of 9 mm and with heated length of 18cm. The reactors were heated resistively with a tube furnace designed and built to minimize the heated length.

The temperature of the reactor was monitored by a K-type thermocouple placed in a quartz thermocouple-well and controlled by a temperature controller. Figure 1 shows a schematic of the flow

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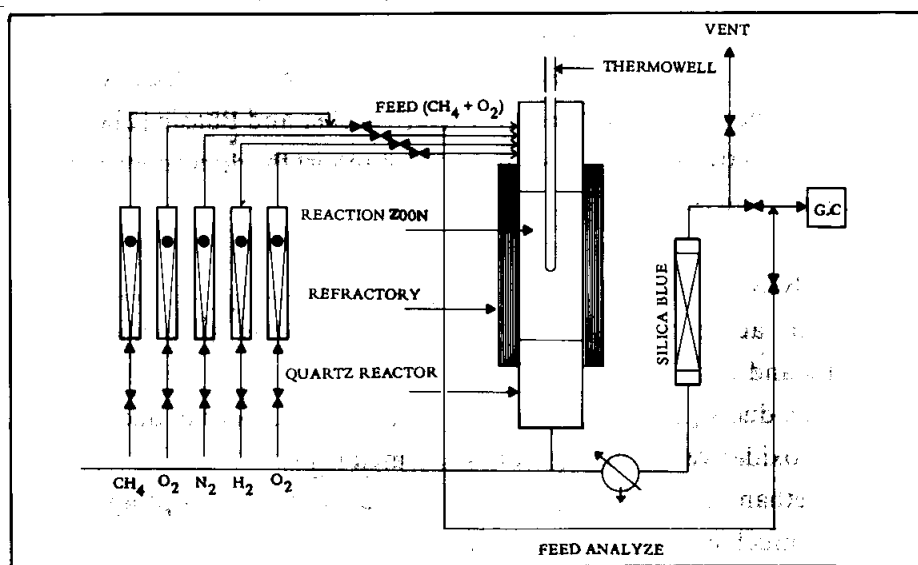


Figure 1. A schematic diagram of the experimental apparatus.

apparatus that was used for the experiments being reported.

The flow rate of each component in the feed was controlled and regulated by electronic mass flow controllers (Brooks Instrument Co.). The delivered gases were used without purification, and were of the following purities: CH₄ (99.99%), O₂ (99.99%), He (99.999%) and N₂ (99.99%). Product analyses were performed by on-line gas chromatography (GC) using a thermal conductivity detector on a Shimadzu GC (Model 6-A) equipped with thermistors.

Water was removed from the reaction products by a trap placed at the reactor exit path to eliminate the presence of a broad water peak from the GC analysis. The major products were C₂H₆, C₂H₄, CO, CO₂, H₂ and H₂O. Two columns were operated in parallel to achieve sufficient separation of the products and reactants. A Q polymer-packed column (1/8" x 12) was used for the separation of CO₂, C₂H₆, C₂H₄ and C₃⁺ hydrocarbons, and a molecular sieve (13x)—packed column (1/8" x 6) was used for separation of H₂, O₂, CH₄ and CO.

The catalysts were prepared by using standard impregnation techniques. In most preparation steps, nitrate salts were dissolved in deionized water and the resulting solution vacuum impregnated on to the silica aluminium (Silica Alumina Grace, Grade 980, surface area 370 m²/gr). Typically, the impregnated carrier was dried in step at 60°C for 30 min, and 110°C for 2-3 hr. Final heat treatment (calcination) was at 850°C in flowing air for 16 hr. The amount of active elements (Mn) was typically between 10-15 wt% and alkaline metal (Na) was 1 to 5 wt%.

Before measurement of each activity, the catalyst would again be calcined for 2 hours by ramping the temperature from room

temperature to 800°C. The reactor was cooled, and then the reaction gases were mixed and fed to the reactor.

A sample was taken at room temperature and then the reactor temperature was ramped to the reaction temperature by using the programmable temperature controller.

RESULTS AND DISCUSSION

It has been shown that the preparation of the catalyst is the most critical part of the procedure. Several catalysts with different materials and various percentages of components have been tested. The following catalysts have presented the most favorable results. Their characteristics are as follows.

The content of promotor in all catalysts are the same, but the active metal content in catalyst No. MTE-101 and MTE-102 is different. The difference between the MTE-103 and MTE-104 is due to the calcination procedure. The MTE-103 was calcined by a tubular furnace in flowing oxygen at 850°C, but the MTE-104 was calcined in a box furnace. In preparing the MTE-105 catalyst, in order to increase the solution of sodium salt, the reaction medium was acidified by nitric acid drops. The effect of a series of parameters has been studied and the optimum conditions for each catalyst have been obtained.

Table 1 illustrates the range of variation of governing parameters for all of the catalysts. Figures 2(a), 2(b) and 2(c) compare the conversion, product selectivity and hydrocarbon yield for each of the catalysts, respectively. Each of these catalysts was pretreated in the flowing O₂ for 2 hours at 800°C before activity measurements were begun.

The results presented in Figure 2 are at the standard set of operating conditions and

Table 1. Summary of the Range of Governing Parameters such as Gas Flow Rate (50-150 cc/min), Oxygen Concentration (10-35%) and Reactor Temperature (600-900°C) Which Have Been Varied to Investigate the Catalyst Activity. It Refers to 3 ml of Catalyst in Reactor, GHSV (Gas Hourly Space Velocity) and W/F (Catalyst Weight Over Flow Rate Ratio) Have Also Been Modified.

| FLOW CC/MIN | O ₂ (%) | TEMP. (°C) | GHSV hr ⁻¹ | W/F Sec |
|-------------|--------------------|------------|-----------------------|---------|
| 50 | 10 | 600-900 | 1000 | 3.6 |
| 50 | 20 | 600-900 | 1000 | 3.6 |
| 50 | 30 | 600-900 | 1000 | 3.6 |
| 50 | 35 | 600-900 | 1000 | 3.6 |
| 100 | 10 | 600-900 | 2000 | 1.8 |
| 100 | 20 | 600-900 | 2000 | 1.8 |
| 100 | 30 | 600-900 | 2000 | 1.8 |
| 100 | 35 | 600-900 | 2000 | 1.8 |
| 150 | 10 | 600-900 | 3000 | 1.2 |
| 150 | 20 | 600-900 | 3000 | 1.2 |
| 150 | 30 | 600-900 | 3000 | 1.2 |
| 150 | 35 | 600-900 | 3000 | 1.2 |

were analyzed after five hours of time-on-stream. As Mn loading increased, the conversion of CH₄ increased. Figures 2(a) — (b) — (c) show that the catalyst MTE-104 gives higher conversion and selectivities which result in a better yield at these operating conditions. Since the MTE-104 catalyst appeared to have some feature necessary for oxidative coupling, the effects of temperature on conversion and selectivity were studied for three months.

Product selectivity and hydrocarbon yield are shown in Table 2 and Figures 3(a), 3(b), and 3(c). As shown in Figure 3(a), as the temperature increased the oxygen conversion also increased, and at 850°C the conversion is completed. Methane conversion will reach its maximum at 830°C.

As shown in Figure 3(b) the CO₂ product

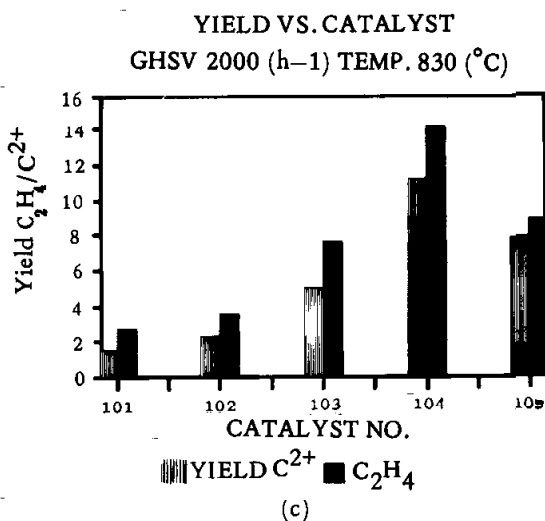
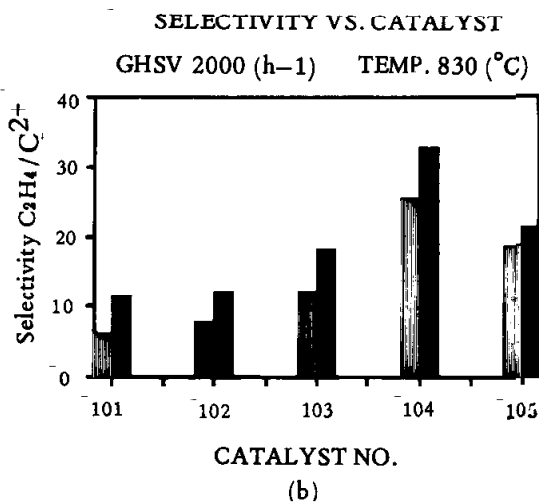
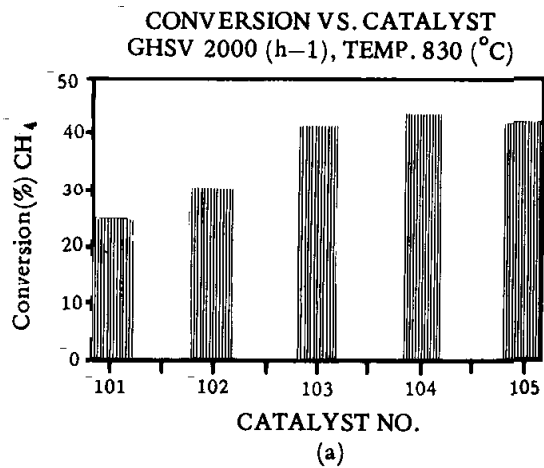


Figure 2. Comparison of conversions, selectivities and yields of several catalysts. The result represents samples taken at five hour time-on-stream with a CH₄/O₂ feed mole ratio of 3, a feed flow rate of 100cc/min, a 3cc catalyst sample, and a temperature of 830°C.

Table 2. The Effect of Temperature on Conversion, Selectivity and Yield for with Feed Mole Ratio (CH₄/O₂) of 3,3^{cc} Catalyst Sample and Feed Flow Rate of 100 cc/min (MTE-104 Catalyst)

| FLOW (CC/MIN.) | TEMP °C | FEED(%) | | CONVERSION(%) | | SELECTIVITY(%) | | | | YIELD C ₂ H ₄ |
|-------------------|------------|----------------|-----------------|-----------------|----------------|-------------------------------|-----------------|-----------------|-------|--|
| | | O ₂ | CH ₄ | CH ₄ | O ₂ | C ₂ H ₄ | C ²⁺ | CO ₂ | CO | |
| 100 | 650 | 32.86 | 67.14 | 34.89 | 63.85 | 0.00 | 0.00 | 63.53 | 23.93 | 0.0 |
| 100 | 730 | 32.86 | 67.14 | 39.29 | 98.82 | 10.84 | 15.60 | 40.59 | 36.51 | 4.3 |
| 100 | 750 | 32.86 | 67.14 | 40.33 | 99.29 | 11.86 | 17.00 | 38.67 | 34.30 | 4.8 |
| 100 | 755 | 32.86 | 67.14 | 40.39 | 97.54 | 11.98 | 16.72 | 38.92 | 34.67 | 4.8 |
| 100 | 800 | 32.32 | 67.68 | 40.08 | 89.69 | 9.93 | 16.16 | 31.29 | 40.03 | 4.0 |
| 100 | 809 | 32.32 | 67.68 | 35.10 | 79.40 | 11.78 | 20.43 | 21.64 | 40.76 | 4.1 |
| 100 | 809 | 32.32 | 67.68 | 35.06 | 78.77 | 11.60 | 20.18 | 20.61 | 43.21 | 4.1 |
| 100 | 810 | 31.98 | 68.02 | 42.31 | 58.07 | 25.28 | 32.71 | 6.64 | 36.03 | 10.7 |
| 100 | 815 | 31.98 | 68.02 | 43.67 | 61.83 | 25.83 | 32.78 | 6.60 | 40.22 | 11.3 |
| 100 | 830 | 31.98 | 68.02 | 52.47 | 75.59 | 22.37 | 27.16 | 5.77 | 36.51 | 11.7 |
| 100 | 840 | 31.98 | 68.02 | 50.19 | 83.12 | 10.15 | 14.88 | 7.91 | 46.35 | 5.1 |
| 100 | 850 | 32.23 | 67.77 | 44.67 | 88.39 | 12.82 | 18.33 | 13.17 | 45.17 | 5.7 |
| 100 | 855 | 32.23 | 67.77 | 45.02 | 88.62 | 12.59 | 18.27 | 12.15 | 43.70 | 5.7 |
| 100 | 860 | 32.23 | 67.77 | 47.04 | 92.01 | 11.63 | 15.80 | 11.72 | 45.87 | 5.5 |
| 100 | 875 | 32.23 | 67.77 | 48.59 | 95.21 | 11.73 | 16.01 | 12.35 | 46.30 | 5.7 |
| 100 | 880 | 32.23 | 67.77 | 47.60 | 95.74 | 11.76 | 15.77 | 13.19 | 44.58 | 5.6 |
| 100 | 905 | 32.23 | 67.77 | 50.08 | 98.44 | 10.90 | 12.94 | 14.23 | 46.28 | 5.5 |

Table 3. Activity and Maximum Selectivity and Yield, for the Oxidative Coupling of Methane Over Catalyst No. MTE-105.

| GHSV (h ⁻¹) | O ₂ (%) | TEMP. °C | CONV. (%) CH ₄ | SELECTIVITY (%) | | YIELD (%) | |
|----------------------------|--------------------|-------------|------------------------------|-------------------------------|-----------------|-------------------------------|-----------------|
| | | | | C ₂ H ₄ | C ²⁺ | C ₂ H ₄ | C ²⁺ |
| 1000 | 10 | 830 | 26 | 14.7 | 17.2 | 3.8 | 4.5 |
| 1000 | 20 | 830 | 23.3 | 17.4 | 20.5 | 4 | 4.8 |
| 1000 | 30 | 820 | 38.5 | 16.8 | 18.3 | 6.3 | 7.1 |
| 1000 | 35 | 830 | 48 | 12.7 | 13.6 | 6.1 | 6.5 |
| 2000 | 10 | 850 | 13.6 | 28.6 | 35.9 | 3.9 | 4.9 |
| 2000 | 20 | 900 | 29.2 | 18 | 19.6 | 5.3 | 5.7 |
| 2000 | 30 | 835 | 41.9 | 18.6 | 21.3 | 7.8 | 8.9 |
| 2000 | 35 | 810 | 34.6 | 12.6 | 16 | 4.4 | 5.6 |
| 2000 | 10 | 855 | 20.7 | 20.2 | 25 | 4.2 | 5.2 |
| 3000 | 20 | 835 | 31.1 | 25.6 | 32.4 | 8 | 10 |
| 3000 | 50 | 830 | 37.6 | 19.5 | 23.9 | 7.3 | 9 |
| 3000 | 35 | 820 | 45.7 | 17.6 | 22.8 | 8 | 10.4 |

Table 4. Summary of Results and Characteristics for Different Catalysts

| CAT NO. | MN(%) | Na ₄ P ₂ O ₇ (%) | SUP MESH SIZE | CON. (%) CH ₄ | SELECTIVITY (%) | | YIELD (%) C ²⁺ |
|---------|-------|---|---------------|--------------------------|-------------------------------|-----------------|---------------------------|
| | | | | | C ₂ H ₄ | C ²⁺ | |
| MTE-101 | 10 | 5 | 30-35 | 25 | 6.2 | 11.2 | 4.75 |
| MTE-102 | 10 | 5 | 30-35 | 30.2 | 7.8 | 12.4 | 5.6 |
| MTE-103 | 10 | 5 | 30-35 | 41 | 12.3 | 18.4 | 7.6 |
| MTE-104 | 10 | 5 | 30-35 | 43.7 | 25.8 | 32.8 | 14.3 |
| MTE-105 | 13 | 5 | 30-35 | 41.9 | 18.6 | 21.3 | 8.9 |

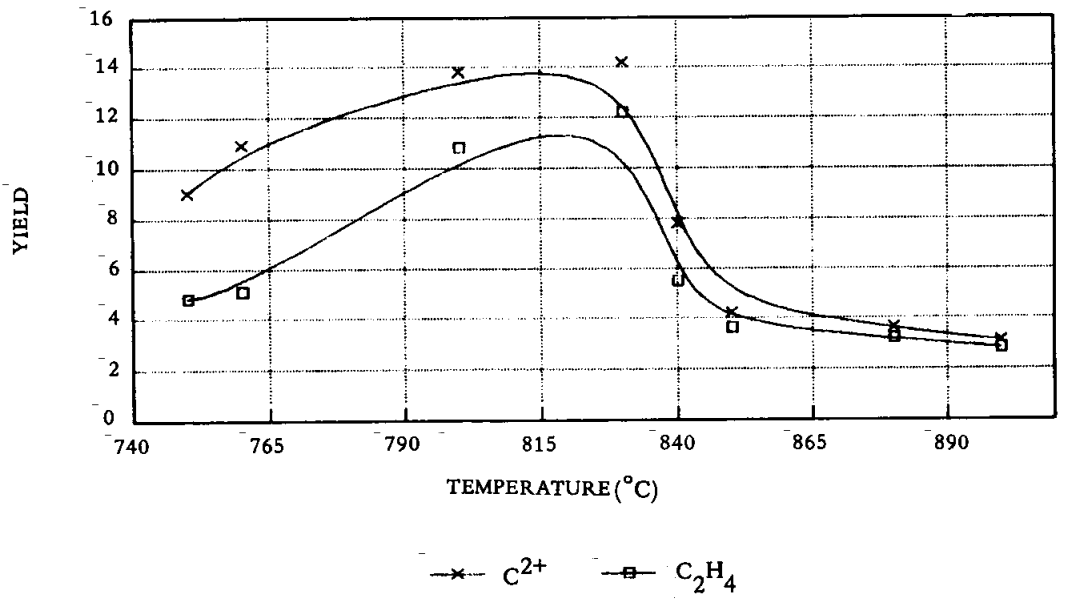
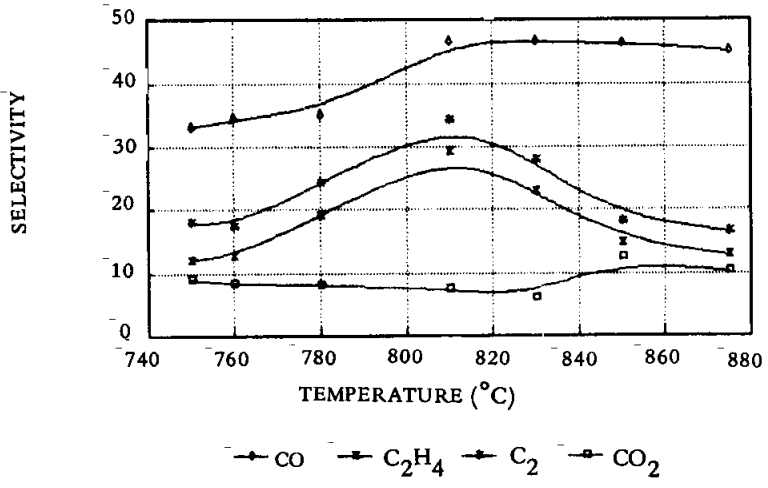
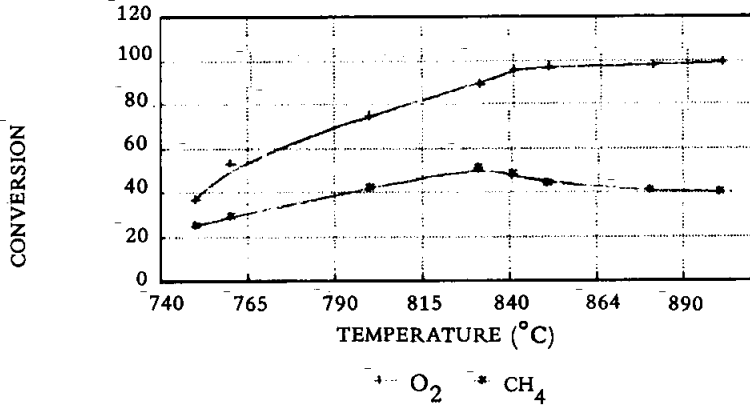


Figure 3. A comparison of the effects of temperature on conversions, selectivity and yield for a feed flow rate of 100 cc/min and a feed mole ratio (CH₄/O₂) of 3.

selectivity decreased with increasing temperature probably due to high oxygen conversion. At these conditions, the catalyst gave slightly higher conversions, but lower product selectivities resulting in lower yields.

Table 5. Summary of Physical and Chemical Characteristics for the Catalyst No. MTE-104.

| | | |
|-------------------|--|--------|
| Surface area | 2 m ² /gr | method |
| App. density | 1 gr/ml | BET |
| Void Volume | 0.05 | He-Hg |
| Particle size | 30-35 mesh | He-Hg |
| Active metal | 14.82% Mn | AAs |
| Promoter | 4.86% Na ₄ P ₂ O ₇ | " |
| Support | 74.83% SiO ₂ | " |
| | 18.54 Al ₂ O ₃ | " |
| Crystal Structure | Mn ₂ O ₃ .γ-Al ₂ O ₃ | X-Ray |

The selectivity of C₂H₄ and C₂⁺ hydrocarbons increased with increasing temperature up to 815°C then decreased.

Figure 3 (c) shows that the C₂H₄ and C₂ hydrocarbons yield increased with increasing temperature up to 830°C, then decreased. Table 3, summerizes the results of the residence time effect, oxygen percent in feed and temperature for MTE-105 catalyst that is not favorable.

Tables 4 and 5 summerize some of the different characteristics of the catalysts and their obtained results.

CONCLUSION

It has been shown that in preparing the manganese oxide catalyst, precise control of operating conditions such as temperature, agitation speed, reactant composition, concentration, and calcination process has considerable effect on yield, conversion and selectivity of the catalyst.

The experiment also reveals that catalysts were found to be highly selective in the temperature range 800 to 830°C, but the selectivity decreased above 830°C. The optimum condition is 830°C and the highest yield for ethylene and C₂⁺ are 11.7% and 14.3%, respectively.

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