Partial oxidation of ^{13}C-labeled ethylene in methane over Ca/Ni/K catalysts

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The relative reactivity of ethane and ethylene compared to methane over the Ca/Ni/K catalyst was determined. The reactivities are in the order of ethylene > ethane ≫ methane. The catalyst was also studied using temperature-programmed reaction, desorption and decomposition.

Keywords: Catalysis; partial oxidation; oxidative coupling

1. Introduction

The development of an economic process that converts natural gas to gasoline, distillate, or other liquid fuels is absolutely needed. In recent years, there has been considerable effort to develop catalysts for converting natural gas to more useful chemicals and fuels. Oxidative coupling of methane to ethane and ethylene and subsequent conversion of these chemicals to liquid fuel is one approach that has attracted great interest in recent years [1,2]. A key to the success of this technology is developing a catalyst that is able to convert methane selectively into higher hydrocarbons, preferably ethylene.

Despite intensive efforts in this area, little progress has been achieved, mainly because the products of methane conversion are more reactive than methane. Earlier reports indicate [3]: (1) the activation of methane occurs both in the gas phase and on the surfaces of the catalyst; (2) in the gas phase, methane is possibly activated by diatomic oxygen; (3) carbon monoxide formed in the gas phase is converted to CO_2 in the presence of catalysts; and (4) surface reactions are important in oxidizing the intermediates CH_3, C_2H_4, C_2H_6, and CO to carbon dioxide. These results show that the overall reaction mechanism is a mixture of homogeneous and heterogeneous reactions. Consequently, it is difficult to change the product distribution entirely by tailoring the catalyst.

In order to minimize gas phase contributions, several research groups have

synthesized catalysts that are active at lower temperatures (<650°C). Pereira et al. reported that catalysts containing calcium, nickel, and potassium oxides convert methane, in the presence of steam, to C_2, C_3, and C_4 paraffins and olefins with about 100% selectivity at <600°C [4].

Dooley and Ross have also conducted experiments using the same type of catalyst [5]. Both studies agreed that addition of steam to the feed significantly increases the C_{2+} selectivity. However, the role of steam and the mechanism of the reaction is unknown. Furthermore, the high C_{2+} selectivity reported by Pereira et al. [4] and Rasko et al. [6] was not reproduced by Dooley and Ross. The objective of this study was to prepare, test, and further characterize the Ca/Ni/K catalyst.

2. Experimental

A catalyst containing calcium, nickel, and potassium (Ca/Ni/K = 2 : 1 : 0.1) was prepared according to the procedure reported by Pereira et al. [4]. A 0.3 m long quartz reactor tube (6.35 mm o.d., 4.0 mm i.d.) with a quartz thermocouple well was used as a fixed-bed reactor with 0.5 g of catalyst (−28/ + 48 mesh) held in place by quartz wool [3].

Temperature-programmed reaction (TPR) was performed on fresh catalyst by passing (total flow of 17.5 cm^3/min) a mixture of oxygen, ^{13}C-labeled ethylene in methane, and helium over the catalyst and raising the temperature from 450°C to final temperatures of 700 or 800°C with a heating rate of 40°C/min. The hydrocarbon-to-oxygen ratio was 2 : 1 and the products were analyzed by on-line gas chromatography equipped with a mass selective detector.

Temperature-programmed desorption/decomposition was performed following the reaction and raising the temperature from 400°C to a final temperature of 700°C with a heating rate of 40°C/min. Helium was used for carrier gas at 40 cm^3/min NPT (20°C and 760 Torr) flow rate.

3. Results and discussion

Partial oxidation of methane was conducted in the presence and absence of steam over two catalysts. One was prepared and pretreated with oxygen for 48 h in our laboratory according to the procedure reported by Pereira et al. [4]. The other potassium-rich catalyst (IDP12) was obtained from Dr. Perry of Lawrence Berkeley Laboratory and was also pretreated with oxygen. The catalysts were tested at temperatures 600–700°C. The hydrocarbon-to-oxygen ratios were varied from 2 : 1 to 3 : 1 and the water flow rates were varied from 1.2 to 4 cm^3/h. The major products were ethylene, ethane, carbon monoxide, and carbon dioxide. In the absence of steam no significant amount of C_2 products were observed. Contrary to the results reported [4,6], in all conditions, carbon dioxide was the major

product. In agreement with results reported by Dooley and Ross [5], we were not able to reproduce the high C_2 selectivity reported by Pereira et al. [4] and Rasko et al. [6]. However, the catalysts appeared to be unstable and the conversion and selectivity varied with time. The highest C_2 selectivity observed was about 52% at 650°C and the highest C_2 yield was about 11% at 675°C. A large variation in the ethylene-to-ethane ratio was also observed ranging from 0.2 to 1.2. The higher ethylene-to-ethane ratio correlates very well with the higher concentration of steam in the reactor. As the temperature increased from 600 to 700°C, the concentration of ethane and ethylene increased while the concentration of carbon oxides decreased as shown in table 1. A test was conducted for 32 h at 680°C. As the reaction time increased the methane conversion remained constant, while the concentration of ethane and ethylene decreased and the concentration of carbon dioxide increased. No significant amount of carbon monoxide was detected after the second day. The results of both catalysts and the results reported by Dooley and Ross [5] are in good agreement.

Since there were significant variations in the product distribution at the earlier stages of the reactions, we conducted several temperature-programmed studies and monitored the reaction products. In these experiments, a mixture of ^{13}C-labeled ethylene in methane, oxygen, and helium were passed over the catalyst and the relative reactivity of ethylene compared to methane was measured.

Figs. 1 and 2 show the thermograms of partial oxidation of ^{13}C-labeled ethylene in methane with concentrations of 5.0 and 2.5 vol% ethylene. Approximately all the oxygen was consumed at temperatures above 570°C. The concentration of carbon dioxide was monitored using a mass spectrometer. As the temperature was raised to 700°C, the concentration (arbitrary unit, a.u.) of carbon dioxide also increased. The two sharp peaks (at about 18 min in to the reaction) show that at earlier stages, carbon dioxide reacts with CaO to form calcium carbonate, and after saturation, the carbonate decomposed to CaO and CO_2. Broader peaks were observed when the same mixture was passed over CaO at 800°C as shown in fig. 3.

Table 1
Effect of temperature on conversion and selectivity over Ca/Ni/K catalyst in the presence of steam

	Temperature (°C)		
	600	650	700
conversion (mol%)			
methane	6.7	18.8	21.0
oxygen	25.7	61.2	85.0
product distribution (carbon mol%)			
C_2H_4	2.7	8.0	20.0
C_2H_6	5.5	15.1	19.7
CO	7.1	2.5	0.6
CO_2	84.7	74.4	59.7

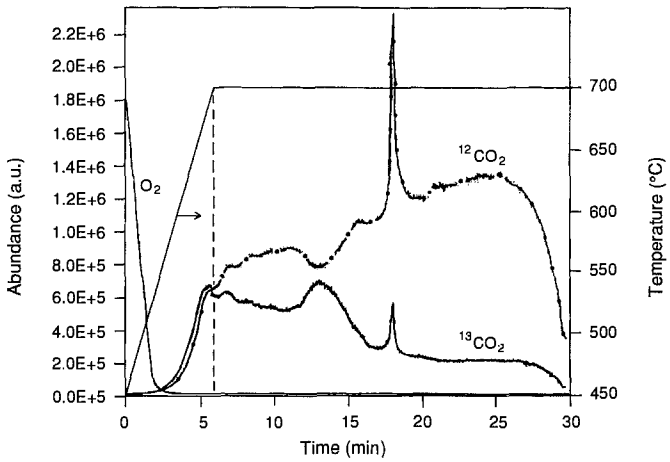

Fig. 1. Thermogram of partial oxidation of ^{13}C-labeled ethylene (5 vol%) in methane over the Ca/Ni/K catalyst.

At earlier stages of reaction, the same amount of carbon dioxide is produced from ethylene (5 vol%) and methane (95 vol%). However, when the concentration of ethylene in methane was reduced to 2.5 vol%, less carbon dioxide was produced from ethylene than from methane. This indicates that the partial pressure of ethylene also plays an important role in earlier stages of the reaction. Although the reactivities of methane and ethylene are different in the earlier stages of reaction, at steady state conditions, both methane and ethylene appear to compete for active centers on the catalyst.

Temperature-programmed desorption of carbon dioxide and carbon monoxide

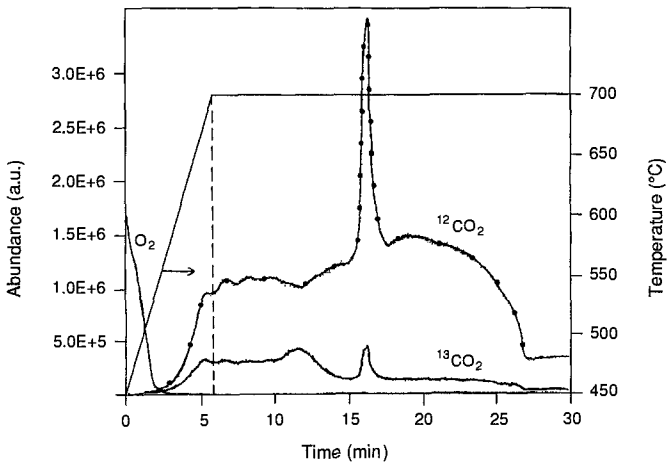

Fig. 2. Thermogram of partial oxidation of ^{13}C-labeled ethylene (2.5 vol%) in methane over the Ca/Ni/K catalyst.

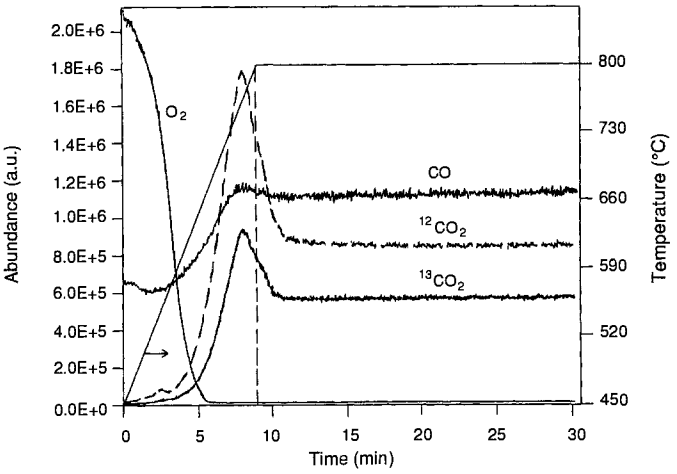

Fig. 3. Thermogram of partial oxidation of ^{13}C-labeled ethylene (5 vol%) in methane over CaO.

from the catalysts after catalytic reactions and decomposition of $CaCO_3$ is shown in figs. 4 and 5. There are at least two peaks for each compound: a relatively sharp peak at about 500°C and a broader peak at a higher temperature. After holding the sample at 700°C for about 15 min, most of the $CaCO_3$ was decomposed. The amounts of CO and CO_2 correlate very well with the amount of CO and CO_2 produced in the reaction. A higher $^{12}CO_2/^{13}CO_2$ ratio was observed for the mixture with 5 vol% compared to that with 2.5 vol% ethylene in methane. Temperature-programmed reaction of pure CaO with CO_2 was also studied by Joly et al. [7]. Two peaks, one at 304°C and the other at 700°C, were observed. The peak at 304°C

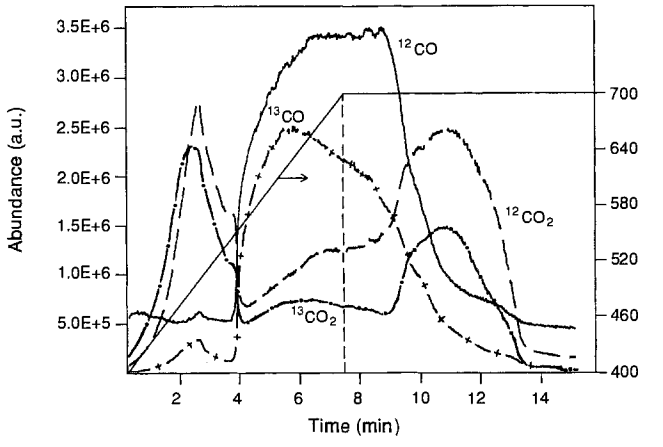

Fig. 4. Temperature-programmed desorption of products from the Ca/Ni/K catalyst after partial oxidation of 5 vol% ethylene in methane.

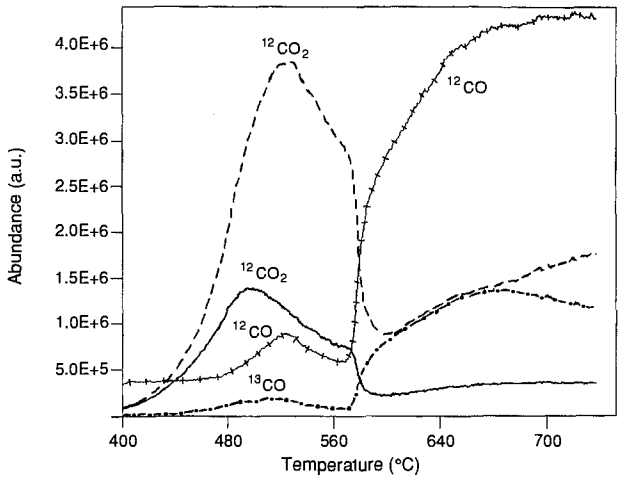

Fig. 5. Temperature-programmed desorption of products from the Ca/Ni/K catalyst after partial oxidation of 2.5 vol% ethylene in methane.

was assigned to CO_2 chemisorption on CaO and the peak at 700°C was assigned to bulk carbonation. The peak for the carbonate decomposition was observed at 910°C. Furthermore, they reported that the position of the peaks shifted to higher temperatures with increasing CaO particle size. Dooley and Ross have also characterized the spent Ca/Ni/K catalyst using X-ray diffraction and detected bulk $CaCO_3$ and K_2CaCO_3 phases [5].

4. Conclusion

Partial oxidation of ^{13}C-labeled ethylene in methane was conducted over the Ca/Ni/K catalyst. Although the results were in good agreement with the results reported by Dooley and Ross [5], we were not able to obtain the high selectivity reported by Pereira et al. [4] and Rasko et al. [6]. The results also indicated that carbon dioxide reacts with calcium oxide at temperatures below 700°C, which then decompose at higher temperatures. The relative reactivity of ethane and ethylene compared to methane over the Ca/Ni/K catalyst was determined. The reactivities are in the order of ethylene > ethane >> methane.

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