Effect of methane co-feeding on the selectivity of ethylene produced from oxidative dehydrogenation of ethane with CO_2 over a Ni-La/SiO_2 catalyst

Xiaoxi Peng,   Jianqiang Zhu,   Lu Yao,   Changwei Hu[*]

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China

Abstract

A Ni-La/SiO_2 catalyst was prepared through the incipient wetness impregnation method and tested in the oxidative dehydrogenation of ethane (ODHE) with CO_2. The fresh and used catalysts were characterized by XRD and SEM techniques. The Ni-La/SiO_2 catalyst exhibited catalytic activity for the oxidative dehydrogenation of ethane, but with low ethylene selectivity in the absence of methane. The selectivity to ethylene increased with increasing molar ratio of methane in the feed. The carbon deposited on the catalyst surface in the sole ODHE with CO_2 was mainly inert carbon, while much more filamentous carbon was formed in the presence of methane. The filamentous carbon was easy to be removed by CO_2, which might play a role in improving the conversion of ethane to ethylene. The introduction of methane might affect the equilibrium of the CO_2 reforming of ethane and the ODHE with CO_2. As a consequence, the synthesis gas produced from CO_2 reforming of methane partly inhibited the reaction of ethane and promoted the ODHE with CO_2, thus increasing the selectivity of ethylene.

Key words

ethane; methane; CO_2; co-activation; Ni-La/SiO_2; ethylene selectivity

1. Introduction

Ethylene is one of the most important bulk industrial materials. It is commonly produced by steam cracking of naphtha [1,2]. However, this process is usually carried out at high temperatures and consumed a large amount of energy [3−5]. Methane and ethane are primary components of natural gas. Attempts in converting these raw materials into more valuable products had been frequently investigated over the last decades. The existed routes for the use of them, such as oxidative coupling of methane (OCM), CO_2 reforming of methane, and oxidative dehydrogenation of ethane (ODHE), all bore some disadvantages [6−11]. Thus, direct co-activation of ethane, methane and CO_2 is of great interest.

In our previous study on OCM, equal molar ratio of ethylene and synthesis gas was obtained with relatively low yields [12−16]. However, besides ethylene and synthesis gas, the effluent also contained C_2H_6, CO_2 and un-converted CH_4. In order to improve the yields of the target products, co-activation of CH_4 and C_2H_6 with CO_2 is essential for an effective utilization of natural gas. Rare earth metals (La, Ce, Y, Sm) were found to modify Ni-based catalysts to attain higher activity and better stability in POM, because the

rare metal oxides improved the dispersion of Ni and inhibited coke formation [17]. In our previous study, high CH_4 conversion and synthesis gas yield were obtained on a Ni-La/SiO_2 catalyst in CO_2 reforming of methane [18]. However, methane could not be coupled to ethylene over such a catalyst with CO_2.

In the present work, we investigated the co-activation of CH_4 and C_2H_6, using CO_2 as an oxidant for the production of ethylene and synthesis gas. The influence of methane introduction on ethylene formation was discussed. This provides an alternative way to utilize natural gas more effectively.

2. Experimental

2.1. Catalyst preparation

In the present work, the Ni(10 wt%)-La(5 wt%)/SiO_2 catalyst was prepared by the incipient wetness co-impregnation method. The SiO_2 support (20−40 mesh, 320 m^2/g, China Medicines Co., Beijing Procurement Supply Station) was impregnated in an aqueous solution with given amount of Ni(NO_3)$_2$ (Chongqing Jiyuan Chemical Company Limited) and (CH_3COO)$_3$La (Alfa Aesar China) for 24 h at room

---

temperature. After being dried at 110 °C for 4 h and calcined at 800 °C for 5 h, the catalyst was cooled down to room temperature for activity test and characterization. The particle size of the catalysts remained to be 20−40 mesh.

2.2. Activity test

The activity test was carried out in a fixed-bed flow quartz-tube reactor. 0.25 g of Ni(10)-La(5)/SiO$_2$ catalyst was loaded in the middle of the reactor and heated from room temperature to reaction temperature (800 °C) under Ar ambience. Then the reactants, C$_2$H$_6$ (99.95%) and CO$_2$ (99.5%) were co-fed into the reactor (120 mL/min, C$_2$H$_6$/CO$_2$ = 1/2). The effect of methane addition on the reaction system was studied by keeping the amount of C$_2$H$_6$ and CO$_2$ constant, and changing the amount of CH$_4$ or Ar added in the system, ranging from 10 to 40 mL/min. The flow rate of the reactant gases (F) were controlled by mass flow controllers. The effluent after removal of water was analyzed by an on-line gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

2.3. Catalyst characterization

The fresh and used Ni(10)-La(5)/SiO$_2$ catalysts were characterized by the XRD technique. The X-ray diffraction patterns were obtained with a DX-1000 CSC diffractometer using Cu K_α monochromatic X-ray (40 kV, 25 mA).

The morphologies of the used Ni(10)-La(5)/SiO$_2$ catalysts were examined by scanning electron microscopy (SEM, FEI Inspect F).

3. Results and discussion

3.1. Activity results

The catalytic activity at 10 h time on stream was listed in Table 1. Ethane conversion of 89.8%, with ethylene selectivity of 23.3% and overall ethylene yield of 20.9%, was obtained in the absence of methane in the feed. Besides ethylene, large amount of synthesis gas was also produced. It indicated that mainly the CO$_2$ reforming of ethane into synthesis gas occurred in this case. On the other hand, with the introduction of methane from 10 to 40 mL/min, methane conversion increased gradually, while the conversions of ethane and CO$_2$ decreased slightly. In contrast, ethylene selectivity increased from 25.3% to 30.5%, along with an increasing amount of methane in the feed. Correspondingly, the yield of ethylene increased from 22.4% to 26.2%.

Table 1. Activity test of Ni-La/SiO$_2$ catalyst

Flow rate of CH$_4$ (mL/min)	Conversion (%)			C$_2$H$_4$ selectivity (%)	C$_2$H$_4$ yield (%)	CO/H$_2$	C Balance	Ni (nm)
	C$_2$H$_6$	CO$_2$	CH$_4$					
0	89.8	64.3	–	23.3	20.9	1.85	75	10.5
10	88.3	62.2	23.4	25.3	22.4	1.81	77	12.3
20	87.7	60.9	29.5	26.4	23.1	1.76	78	13.1
30	86.2	58.7	32.7	28.6	24.7	1.71	79	14.4
40	85.7	57.5	35.2	30.5	26.2	1.62	81	15.6

Reaction condition: molar ratio of C$_2$H$_6$/CO$_2$ = 1/2, F = 120 mL/min, atmospheric pressure, 800 °C, 0.25 g Ni(10)-La(5)/SiO$_2$

As reported in literature [19−21], the reverse water-gas shift (RWGS) reaction was inhibitory in CO$_2$ reforming of methane. On the other hand, in the present system, the WGS would take place to produce extra CO$_2$. As a result, CO$_2$ conversion was actually decreased with the increasing amount of CH$_4$. It can be illustrated by the molar ratio of CO/H$_2$, which dropped from 1.85 to 1.62 with CH$_4$ addition from 10 to 40 mL/min.

Though the conversion of ethane dropped from 89.8% to 85.7%, the overall yield of ethylene raised from 20.9% to 26.2%. According to our previous experiment [18], only synthesis gas could be produced in CO$_2$ reforming of methane on the Ni-La/SiO$_2$ catalyst at 800 °C. Therefore, ethylene might be produced only from ethane dehydrogenation, rather than from oxidative coupling of methane by CO$_2$. The synthesis gas produced from CO$_2$ reforming of methane might affect the equilibrium of the ethane oxidative dehydrogenation and the CO$_2$ reforming of ethane. However, the CO$_2$ reforming of ethane into synthesis gas would be inhibited more significantly than the oxidative dehydrogenation into ethylene.

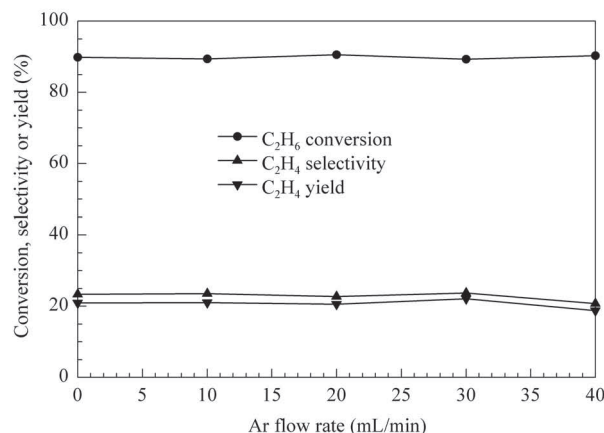As a result, the selectivity to ethylene increased from 23.3% to 30.5%.

Figure 1. The activity of the catalyst in the presence of Ar. Reaction conditions: molar ratio of C$_2$H$_6$/CO$_2$ = 1/2, F = 120 mL/min, 800 °C, flow rate of Ar = 0∼40 mL/min