

Cofeeding of Methane and Ethane to Produce Syngas over a LiLaNiO/ γ -Al₂O₃ Catalyst

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Abstract: Partial oxidation of methane and ethane to syngas over a LiLaNiO/ γ -Al₂O₃ catalyst was investigated with a flow-reactor, XPS and XRD. Excellent reaction performance for CH₄-C₂H₆-O₂ to syngas over the LiLaNiO/ γ -Al₂O₃ catalyst was achieved at 1073K, obtaining CO selectivity of 90%-95% and CH₄ conversion of ~ 97%, with a wide range of C₂H₆ content in the feed and of space velocity.

Keywords: partial oxidation, cofeeding of methane and ethane, syngas, LiLaNiO/ γ -Al₂O₃.

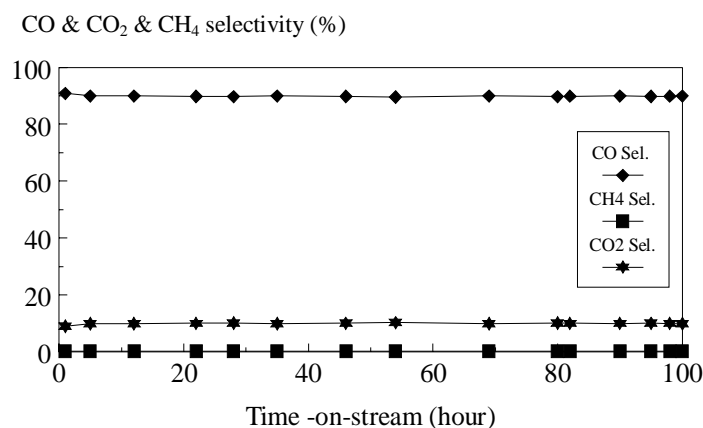
There are abundant supplies of mixture gases containing CH₄ and C₂H₆ from natural gas, FCC (Fluidized Catalytic Cracking) dry gas, refinery gas, *etc.* Commonly, the amount of C₂H₆ is relatively lower than that of CH₄. With regard to the utilization of methane, partial oxidation of methane to syngas over nickel based catalysts has received intensive attention^{1,2}. For mixture gases containing CH₄ and C₂H₆, their conversion to syngas is also of significance (but has not gained adequate attention), because a complete separation of ethane from methane may not be economical³. Schmidt *et al.*^{4,5} reported that syngas could be produced from CH₄, C₂H₆ and C₃H₈ respectively, over a supported Rh catalyst with high selectivity and conversion. However, few studies of cofeeding of methane and ethane to syngas reported. We first reported here the reaction performance of nickel based catalysts for CH₄-C₂H₆-O₂ to syngas. Previously, Xiong *et al.*⁶ reported a good catalyst-LiLaNiO/ γ -Al₂O₃ for the partial oxidation of methane to syngas. From the results of Xiong⁶, it can be concluded that the catalyst has the advantages of high selectivity to syngas and high carbon-deposition resistance. The results implied that LiLaNiO/ γ -Al₂O₃ might be an effective catalyst for CH₄-C₂H₆-O₂ to syngas. In this letter, the reaction performance of LiLaNiO/ γ -Al₂O₃ for CH₄-C₂H₆-O₂ to syngas was investigated.

Preparation of LiLaNiO/ γ -Al₂O₃ has been described previously². Catalysts were tested by flow-reaction in atmospheric pressure fixed-bed microreactor. Products of the reaction were analyzed by gas chromatography using a TCD detector. Conversion and selectivity were calculated on the basis of carbon numbers of the feed reacted.

XPS characterization was performed using a VG RSCA LABMK II spectrometer. XRD characterization was performed with a Rigaku D/Max-RB X-ray diffractometer using a copper target at 40kV x 100mA and scanning speed of 8°/min.

The reaction performance of LiLaNiO/ γ -Al₂O₃ for partial oxidation of ethane (POE) to syngas was investigated. The results were shown in **Figure 1**. Under the conditions of reaction temperature at 1123K, O₂/C₂H₆/He ratio of 1.10/1/4 and space velocity 7×10^4 L/(kg.h), C₂H₆ and O₂ conversions were >99.9%, no C₂H₄ appeared in the products, CO and CO₂ selectivity were ~90%, ~10% respectively, during the 100h of operation. These results indicated that the LiLaNiO/ γ -Al₂O₃ catalyst was an effective POE reaction catalyst during the high temperature reaction.

Figure1. Reaction performance of LiLaNiO/ γ -Al₂O₃ as a function of time (O₂/C₂H₆/He=1.1/1/4; SV= 7×10^4 L/(kg.h); T=1123K)



Under the constant space velocity by keeping the flow rate of CH₄ (70ml/min) and the total flow rate (205ml/min) of C₂H₆, O₂ and He constant, the respective flow rates of C₂H₆, O₂ and He were changed to obtain different CH₄/C₂H₆/O₂ ratios. The effect of CH₄/C₂H₆/O₂ ratio on the reaction performance of the LiLaNiO/ γ -Al₂O₃ was carried out (**Table 1**). The results showed that the catalyst could maintain excellent selectivity to syngas with a wide range of C₂H₆ content in the feed (CO and H₂ selectivity were ~93% and ~99%, respectively). Furthermore, The results (**Table 1**) indicated that the influence of space velocity was not appreciable, *i. e.*, the LiLaNiO/ γ -Al₂O₃ kept good reaction performance with a wide range of space velocity.

Table 1. Effect of CH₄/O₂/C₂H₆ ratio on the reaction performance of LiLaNiO/ γ -Al₂O₃ (SV= 1.65×10^5 L/(kg.h); SV_{CH₄}= 4.2×10^4 L/(kg.h); T=1073K)

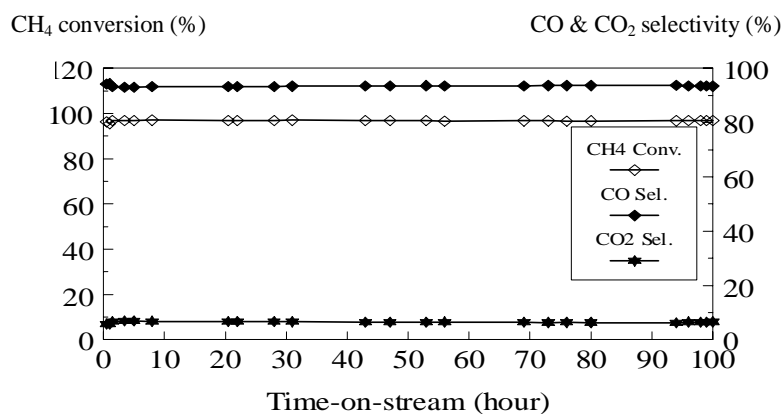
Feed composition			Reaction performance			
CH ₄ %	O ₂ %	C ₂ H ₆ %	XCH ₄ %	SCO %	SCO ₂ %	SH ₂ %
55.0	36.5	8.5	97.6	94.5	5.5	99.0
45.9	39.3	14.8	97.4	93.7	6.3	99.2
39.5	40.8	19.7	96.8	93.3	6.7	99.0
39.5	40.8	19.7 ⁽¹⁾	98.1	94.4	5.6	99.5
39.5	40.8	19.7 ⁽²⁾	98.5	95.2	4.8	99.8
34.8	43.4	21.8	97.8	90.9	9.1	97.3
30.8	43.9	25.3	96.8	91.9	8.1	98.5

In all cases, O₂ and C₂H₆ conversions were > 99.9%

- (1) $SV=3.3 \times 10^5 \text{ L}/(\text{kg}\cdot\text{h})$; $SV_{\text{CH}_4}=8.4 \times 10^4 \text{ L}/(\text{kg}\cdot\text{h})$
 (2) $SV=6.6 \times 10^5 \text{ L}/(\text{kg}\cdot\text{h})$; $SV_{\text{CH}_4}=1.7 \times 10^5 \text{ L}/(\text{kg}\cdot\text{h})$

In order to examine the stability of LiLaNiO/ γ -Al₂O₃ for CH₄-C₂H₆-O₂ to syngas reaction, the 100h life test experiment was performed (**Figure 2**). During the 100h of operation, methane conversion kept ~97% (C₂H₆ and O₂ conversions were >99.9%), no C₂H₄ appeared in the products, CO and CO₂ selectivities were ~93%, ~7%, respectively. These results indicated that the LiLaNiO/Al₂O₃ catalyst was also a good CH₄-C₂H₆-O₂ reaction catalyst during the high temperature reaction.

Figure 2. Reaction performance of LiLaNiO/ γ -Al₂O₃ as a function of time (CH₄/O₂/C₂H₆/He=39.0/41.2/19.8/74; $SV=1.65 \times 10^5 \text{ L}/(\text{kg}\cdot\text{h})$; $T=1073\text{K}$)



After the 100 h of operation, the used catalysts were cooled to room temperature in a flow of N₂, then characterized by XRD and XPS. XRD results revealed that the reduced nickel was present in the used catalyst. γ -Al₂O₃ phase was present before reaction. After operation, γ -Al₂O₃ phase in the LiLaNiO/ γ -Al₂O₃ has hardly undergone phase transformation to α -Al₂O₃ phase. The results revealed that the catalyst had stable crystal phase structure and the reduced nickel was necessary for CH₄-C₂H₆-O₂ to syngas reaction.

Carbon-deposition of the used catalyst was characterized with XPS. The results indicated that the intensity of the graphitic or carbidic surface carbon peak for the used LiLaNiO/ γ -Al₂O₃ was similar to that for the fresh one, *i.e.*, the used catalyst had hardly any carbon-deposition. It can be concluded from the results that the LiLaNiO/ γ -Al₂O₃ catalyst has high carbon-deposition resistance during the high temperature reaction.

Longer life test for CH₄-C₂H₆-O₂ to syngas over the LiLaNiO/ γ -Al₂O₃ catalyst and mechanism of the reaction are still in progress.

References

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